PB84-162726

Ecosystem Responses to Alternative Pesticides in the Terrestrial Environment A System Approach

Michigan State Univ., East Lansing

Prepared for

Corvallis Environmental Research Lab., OR

Aug 83

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-162726

EPA-600/3-83-079a
August 1983

ECOSYSTEM RESPONSES TO ALTERNATIVE PESTICIDES IN THE TERRESTRIAL ENVIRONMENT:
A SYSTEM APPROACH

Erik D. Goodman
Department of Electrical Engineering and Systems Science

Matt Zabik
Jeffrey J. Jenkins
Robert M. Kon
Pesticide Research Center

Renate M. Snider
Department of Zoology
Michigan State University
East Lansing, Michigan

R-805624

Project Officer

Jay D. Gile
Toxics and Hazardous Materials Branch
Environmental Research Laboratory
Corvallis, Oregon 97333

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OREGON 97333

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-83-079a	2. EPA/DF-84/001a	3. RECIPIENT'S ACCESSION NO. PB84-162726
4. TITLE AND SUBTITLE Ecosystem Responses to Alternative Pesticides In the Terrestrial Environment: A System Approach		5. REPORT DATE August 1983
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Erik D. Goodman, Matt Zabik, Jeffrey J. Jenkins, Robert M. Kon, Renate M. Snider		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Michigan State University East Lansing, Michigan		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. R-805624
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Corvallis, Oregon 97333		13. TYPE OF REPORT AND PERIOD COVERED Final Project Report
		14. SPONSORING AGENCY CODE EPA/600/02

15. SUPPLEMENTARY NOTES for magnetic tape see PB84-162734

16. ABSTRACT

A conceptual model was developed to describe aspects of the fate and effects of a pesticide in an orchard ecosystem. In order to refine, parameterize, and test a mathematical model based upon this conceptual model a program of field and laboratory experiments was undertaken. The environmental behavior of azinphosmethyl was studied in a Michigan apple orchard watershed to gather data for the model on initial distribution within the orchard, vertical movement of the pesticide under the influence of rainfall, loss from the orchard with runoff, and the effects of the pesticide on several invertebrate populations. The estimated proportion of a low-volume application initially distributed within the orchard averaged .624 (standard deviation of .149) over three seasons (1976-1978). Examination of residues reaching each layer showed the majority of the dislodgeable residues were distributed to the trees and grass-broadleaves. The litter-moss and soil contained residue levels roughly ten times lower than tree leaf residues. Runoff studies indicated loss, via this route of less than 1% azinphosmethyl residues present in the orchard. The generalized model developed, entitled the Pesticide Orchard Ecosystem Model (POEM), includes as a special case the model for the azinphosmethyl applications under the conditions of this field study. POEM also includes facilities for altering parameters to describe effects of other formulations, other pesticides, other application procedures and/or other field conditions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 305
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

Although the research described in this report has been funded by the U.S. Environmental Protection Agency through Cooperative Agreement number R-805624 to Michigan State University, it has not been subjected to the Agency's peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

CONTENTS

Page

Disclaimer ii

Table of Contents iii

Figures iv

Tables xii

Summary and Recommendations xvii

Acknowledgement xiv

Introduction xx

CHAPTERS

I Experimental Data for the Azinphosmethyl Fate Model 1

II Parameterization of the Azinphosmethyl Fate Model 32

III Airborne Loss from the Orchard 54

IV Generalization of the Pesticide Fate Model 84

V Field Studies of Azinphosmethyl (Guthion^R) Effects on Soil/Litter Invertebrates 115

VI Laboratory Toxicity Studies on Selected Soil/Litter Invertebrates 122

VII Descriptions of Spider, Earthworm, and Springtail Models .. 132

VIII The Ecobiology of Trachelipus Rathkei 135

IX The Effects of Azinphosmethyl on a Population of *Trachelipus rathkei* (Isopoda) 156

X A Study and Model of Azinphosmethyl Effects on a Population of T. rathkei 164

References 194

Appendices

A. Running the Process and Orcdata Data Analysis Routines A-1

B. The POEM Model User's Guide B-1

FIGURES

Number		Page
I-1	Orchard plots	4
I-2	Overhead view of horizontal regions of orchard plots	6
I-3(a-d)	Azinphosmethyl dislodgeable and soil residues for the canopy region, 1976 season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line	22
I-3(e-g)	Azinphosmethyl dislodgeable and soil residues for the alley region, 1976 season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line	23
I-4(a-d)	Azinphosmethyl dislodgeable and soil residues for the canopy region, 1977 season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line	26
I-4(e-g)	Azinphosmethyl dislodgeable and soil residues for the alley region, 1977 season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line	27
I-5	Daily temperature range, 1976 season	15
I-6	Daily minimum and maximum relative humidity, 1976 season	28

FIGURES

Number Page

I-7 Daily temperature range, 1977 season 29

I-8 Daily minimum and maximum relative humidity, 1977 season 30

II-1 Conceptual model for the distribution, movement, and attenuation of azinphosmethyl in an apple orchard 33

II-2 Flow chart showing data processing to yield files suitable for use in model parameterization 36

II-3 Flow chart of the process of calculating the parameters using the "processed files" 37

II-4 Azinphosmethyl attenuation matrix 40

II-5 Azinphosmethyl non-rainfall movement matrix 41

II-6 Azinphosmethyl light rainfall movement matrix 42

II-7 Azinphosmethyl heavy rainfall movement matrix 43

II-8(a-d) Actual and predicted Azinphosmethyl dislodgeable and soil residues for the canopy region, 1978 season, using predicted initial distribution for each spray period. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (µg/cm^2 ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the residues using 1976 and 1977 data only, while the dashed line shows the predicted residues based on all three years (1976-1978) data 46

II-8(e-g) Actual and predicted Azinphosmethyl dislodgeable and soil residues for the alley region, 1978 season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (µg/cm^2 ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the change in residues using 1976 and 1977 data only, while the dashed line shows the predicted change in residues based on all three years'..... 47

FIGURES

Number		Page
II-9(a-d)	Actual and predicted Azinphosmethyl dislodgeable and soil residues for the canopy region, 1978 season, using the observed initial distribution for each spray period. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$ ground area) is above the line and its corresponding standard error (S.E.) below the line. The line running through the bars represents the model's prediction of the residues using 1976 and 1977 data only, while the dashed line shows the predicted residues based on all three years (1976-1978) data	48
II-9(e-g)	Actual and predicted Azinphosmethyl dislodgeable and soil residues for the alley region, 1978 season, using the observed initial distribution for each spray period. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$ ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the residues using 1976 and 1977 data only, while the dashed line shows the predicted residues based on all three years' (1976-1978) data	49
III-1	Orchard plots showing air sampling locations	56
III-2	Diurnal Azinphosmethyl airborne residues at sampling heights between 0.5 and 6.0 meters above the orchard, measured at the center location during the first spray period of the 1978 season	57
III-3	Diurnal Azinphosmethyl airborne residues at sampling heights between 0.5 and 6.0 meters above the orchard, measured at the downwind locations during the first spray period of the 1978 season	70

FIGURES

Number — Page

III-4(a-d) Azinphosmethyl dislodgeable and soil residues for the canopy region, 1978 season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line 71

III-4(e-g) Azinphosmethyl dislodgeable and soil residues for the alley region, 1978 season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line 72

III-5 Decline in total Azinphosmethyl dislodgeable and soil residues measured during the first spray period of the 1978 season 83

III-6 Decline in total Azinphosmethyl dislodgeable and soil residues measured during the second spray period of the 1978 season 82

III-7 Daily temperature range, 1978 season 61

III-8 Daily minimum and maximum relative humidity, 1978 season 62

IV-1 Azinphosmethyl hydrolysis rate constant versus pH 87

IV-2 Azinphosmethyl hydrolysis rate constant versus air temperature 89

IV-3 Azinphosmethyl hydrolysis rate constant versus soil temperature 90

IV-4 Azinphosmethyl microbial degradation versus soil percent organic matter 91

IV-5 Azinphosmethyl microbial degradation versus soil temperature 94

IV-6 Amitrole degradation versus soil moisture for two soil types 96

FIGURES

Number — Page

IV-7(a-d) Predicted 1978 azinphosmethyl residues in orchard canopy region layers. Dashed lines represent predictions based on standard condition attenuation rates (Table IV-2), while solid lines include predicted effects of daily temperature and soil moisture changes (the "base line run") 104

IV-7(e-g) Predicted 1978 azinphosmethyl residues in orchard alley region layers. Dashed lines represent predictions based on standard condition attenuation rates (Table IV-2), while solid lines include predicted effects of daily temperature and soil moisture changes (the "base line run") 105

IV-8a-d) Predicted effects of lowering daily temperature by 10°F on azinphosmethyl residues (dashed lines) versus the base line run (solid lines) 106

IV-9(a-d) Predicted effects (dashed lines) of increasing pesticide volatilization rate by 10x (from 10^{-7} to 10^{-6} mm Hg). Solid lines are base line run 107

IV-10 Predicted effects (dashed line) of altering soil pH from 7 to 9 108

IV-11(a-d) Predicted effects (dashed lines), in canopy layers, of doubling daily rates of pesticide movement due to heavy and light rainfall. Solid lines represent the base line run 109

IV-11(e-g) Predicted effects (dashed lines), in alley layers, of doubling daily rates of pesticide movement due to heavy and light rainfall. Solid lines represent the base line run 110

IV-12(a-d) Predicted effects (dashed lines), in canopy layers, of postulating no inter-layer pesticide movement under non-rainfall conditions. Solid lines represent the base line run 112

IV-12(e-g) Predicted effects (dashed lines), in alley layers, of postulating no inter-layer pesticide movement under non-rainfall conditions. Solid lines represent the base line run 113

V-1 *T. rathkei* sampled in 1979 in three orchard plots 121

FIGURES

Number		Page
VIII-1	Growth of *Trachelipus* females on two diets (mean weights at 10-day intervals, plus or minus one S.D. at selected ages)	137
VIII-2	First broods of *Trachelipus*: relationship between the post-parturient weight of females and the number of young released ($y = 0.859$ wt $- 6.434$; $r^2 = 0.77$)	140
VIII-3	Second broods of *Trachelipus*: relationship between post-parturient female weight and number of young released ($y = 0.538$ wt $+ 1.154$; $r^2 = 0.47$)	140
VIII-4	Relationship between weight gained during gravidity and the number of young produced. Weight gain = maximum recorded weight - initial gravid weight ($y = 0.264x + 1.154$; $r^2 = 0.47$)	142
VIII-5(a-c)	Mean weights at 10-day intervals of breeding *Trachelipus* females reared at three temperatures. Crosses replacing dots indicate that 40 percent or more of all individuals were carrying broods. At each temperature, the replicates were grouped according to female weights after the first brood release: <30 mg, 30-40 mg, and 50-60 mg. Numbers in parentheses: number of replicates at the beginning of observation	145
VIII-6	Number of days spent by *Trachelipus* females in each of four weight classes, at three constant temperatures	145
VIII-7	Weight distribution of the *Trachelipus* field population, in percent of all females captured per date. Total numbers (in parentheses) include half of the prejuveniles plus all identifiable females caught. Weight class definitions: 1 = 0.5-5.0 mg; 2 = 5.01-30.0 mg; 3 = 30.01-50.0 mg; 4 = >50.0 mg	150
VIII-8	Distribution of the *Trachelipus* population over four weight classes, each divided into the following sub-classes: Class 1: 0.5-0.89; 0.90-2.11; 5.0 mg. Class 2: 5.01-9.79; 9.80-19.17; 19.18-30.0 mg. Class 3: 30.01-35.57; 35.58-42.17; 42.18-50.0 mg. Class 4: 50.01-59.28; 59.29-70.29; >70.29 mg. Data are given as percent of all females caught. Total numbers as in Fig. 7	151

FIGURES

Number		Page
VIII-9	Breeding periodicity of *Trachelipus* in the field: of all females $\geq$ 12 mg, percent in breeding condition. Solid line: females with empty oostegites included; broken line: only individuals actually carrying brood are counted	153
VIII-10	Weight structure of the breeding segment of the *Trachelipus* field population, in percent of the total number of females carrying brood on each collection date	153
IX-1	Mean number of *T. rathkei* collected from boards placed underneath tree canopies and from those in alleys between trees	158
IX-2	Percent females captured, of the total number of *T. rathkei* that could be sexed; exact collection dates as in Fig. 1 Symbols: ○ = Plot 7, X = Plot 8	159
IX-3(A,B)	Size class distribution, in percent of total number captured per date, of *T. rathkei* populations throughout one year. A: control plots 7 and 8 combined. B: sprayed plots 2 and 5 combined. In parentheses: number of animals collected. See text for description of size classes. Errata in fig. 3B. Plot-number above the first column should be read 4 instead of 6. At 07.04.78 61 animals were collected	162
X-1	Conceptual model showing processes affecting a life stage of *T. rathkei*. Solid lines represent flow of *T. rathkei*; dashed lines, flow of information. Valves control rate of flow, based on incoming information	168
X-2	Expanded diagram highlighting the breeding process and the factors affecting it	170
X-3	Expanded view of the life stages of *T. rathkei* as tracked in the model. Each box indicates the number of bins it contains. Individuals may also leave TRBRST 1 and TRBRST 2 (post-parturient "resting" stages) for the top row of non-breeding classes, although the arrows were omitted to simplify the diagram	171

FIGURES

Number Page

X-4 Time response of $C_{i,s}(k)$. Vertical axis shows the proportion of the distance between $C_{i,s}(0)$ and m_i which $C_{i,s}(k)$ has moved by day k, for various choices of A, the daily change rate 180

X-5 Mean numbers of isopods captured/board, in control vs. sprayed plots, broken into size groups of $\leq$ 12 mg, >12 mg 186

X-6 Simulated populations (number/m^2) of *T. rathkei* for three years in a control (unsprayed) plot: (a) eggs (daily hatch), (b) 0.5-5 mg, (c) 5-12 mg, (d) 12-30 mg, (e) 30-50 mg, (f) 50-80 mg, (g) >80 mg, (h) totals, excluding eggs 189

X-7 Simulated populations (number/m^2) of *T. rathkei* for three years in a plot sprayed with azinphosmethyl (see Pesticide Fate Model section): (a) eggs (daily hatch), (b) 0.5-5 mg, (c) 5-12 mg, (d) 12-30 mg, (e) 30-50 mg, (f) 50-80 mg, (g) >80 mg, (h) totals, excluding eggs 190

A-1 Flowchart of the processing of raw data to create processed files A-2

A-2 Data flow in parameterization routines (ORCDATA) A-10

TABLES

Number		Page
I-1	Summary of Significant Events for the Orchard, 1976 Season	8
I-2	Summary of Significant Events for the Orchard, 1977 Season	9
I-3	Azinphosmethyl Initial Horizontal Distribution from the Analysis of Targets, 1976 Season	10
I-4	Azinphosmethyl Initial Horizontal Distribution from the Analysis of Targets, 1977 Season	11
I-5	Initial Vertical Distribution of Azinphosmethyl Dislodgeable Residues (μg/cm^2 + SE)	12
I-6	Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied (± SE), from the Analysis of Samples[a]	14
I-7	Initial Vertical Pesticide Distribution, as a Proportion of the Amount Applied, Using Target Data to Calculate Proportion Reaching the Orchard Floor	17
I-8	Azinphosmethyl in Runoff, 1977 Season	18
II-1	Comparison of the Model Predictions (Including Drift)[a] with Azinphosmethyl Residue Data for the 1978 Season	51
II-2	Comparison of the Model Predictions (Excluding Spray Dates)[a] with Azinphosmethyl Residue Data for the 1978 Season	53
III-1	Summary of Significant Events for the Orchard, 1978 Season	59
III-2	Azinphosmethyl Initial Horizontal Distribution from the Analysis of Targets, First Spray Period of the 1978 Season	63
III-3	Initial Vertical Distribution of Azinphosmethyl Dislodgeable Residues,[a] First Spray Period of the 1978 Season[b]	65
III-4	Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied (± S.E.) from the Analysis of Samples for the First Spray Period of the 1978 Season	66

TABLES

Number		Page
III-5	Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied, Using Target Data to Calculate the Proportion Reaching the Orchard Floor, for the First Spray Period of the 1978 Season	67
III-6	Azinphosmethyl Concentrations ($\mu g/cm^3$) at Sampling Heights Between 0.5 and Six Meters Over Orchard	68
III-7	Estimated Azinphosmethyl Daily Airborne Loss from the Orchard, First Spray Period of the 1978 Season	77
IV-1	Azinphosmethyl Degradation when Incubated with Various Soils[a]	87
IV-2	Daily Azinphosmethyl Attenuation Proportions, Under Standard Conditions, Subject to User Alteration	101
IV-3	Daily Azinphosmethyl Attenuation Proportions, Separated by Process, Under Standard Conditions, Subject to User Alteration	102
V-1	Plots Sampled by Pit-Trapping in 1977-79	116
V-2	Results of Analysis of Variance of Selected Groups of Invertebrates Found in Pit-Trap Samples (NS = Not Significant; Dashes = Factors Not Included in the Statistical Model in 1979)	117
V-3	Mean Number of A. caliginosa Per Sample in 1976 and 1977. Three Samples Were Taken Per Plot. The Figures Include All Worms Found in the Upper 30 cm of Soil (Means ± S.E.)	119
V-4	Average Percent of Worms Found in 3 Depth Increments (Mean ± S.E., Number of Samples in Parentheses) in the 1976 and 1977 Sampling Seasons	119
VI-1	Percent Mortality of Folsomia candida After 6 Days Exposure to Field-Collected, Guthion-Contaminated litter at 21°C. Replication: 10 Individuals per each of 10 replicate containers	123

TABLES

Number Page

VI-2 Percent Mortality of Collembola After 7 Days Exposure to Guthion in Yeast and in Soil at Two Moisture Regimes, at 15.5°C. Replication: 40 Individuals of Each Species in Each of 5 Replicate Containers per Dosage 123

VI-3 Percent Mortality of Collembola After 24 Hours Exposure to Guthion in Soil (25% moisture) and in Yeast, at 15.5°C. Replication: 200 Animals of Each Species per Dosage 124

VI-4 Percent Mortality of *Tidabius tivius* (Chilopoda) After 7 Days on Guthion-Contaminated Soil (25% moisture) at 26.7°C. Replication: 20 Individuals per Stage and Concentration 125

VI-5 Toxicity of Guthion to Adult Isopods at 15.5°C (Soil: 25% Moisture), as Percent Mortality After 7 Days Exposure 126

VI-6 Replication in Diazinon Toxicity Experiments With *T. rathkei*: Numbers of Animals Observed per Weight Bin and ppm Diazinon, at 26.7°C 127

VI-7 Results of GLC Analyses of Diazinon-Contaminated Soil (Adjusted for GLC Extraction Efficiency) Prior to Using the Soils for Toxicity Experiments with *T. rathkei* 128

VI-8 Percent Mortality of *T. rathkei* Exposed to Diazinon-Contaminated Soil at Three Temperatures. Values Not in Parentheses are Cumulative 7-Day Mortalities; Values in Parentheses are 10-Day Mortalities (Same Animals, 3 Days Later). Weight Bins as Specified in Table VI-6 Were Combined Into Larger Weight Classes, to Obtain a Minimum of 5 Replicate Animals per Class 129

VI-9 7-Day Mortality Percentages (Corrected for Control) for *T. rathkei* Reared on Guthion- and Diazinon-Contaminated Soil. Data Included Only if a Minimum of 10 Replicate Test Animals Had Been Observed Per Weight Class and Dosage 130

VI-10 Relative Toxicity of Guthion and Diazinon to *Trachelipus rathkei* at Three Temperatures. For Details See Table VI-8 and Chapter X 131

TABLES

Number		Page
VI-11	Toxicity of Diazinon-Contaminated Soils to II. Instar *Trachelipus rathkei* at 15.6°C, Contrasted to Guthion Toxicity at the same Temperature. All Data Corrected for Control by Abbott's Formula. Replication: Minimum of 40 Animals Per Run, (Two Per Replicate Container)	131
VIII-1	Duration of Gravidity, in Days, of *Trachelipus* Females Kept at Three Temperatures	139
VIII-2	Duration, in Days, of the Rest Interval Between Brood Release and the Next Brood Molt of *Trachelipus*	139
VIII-3	Number of Consecutive Broods Produced by *Trachelipus* Females in the First Breeding Period (Percent in italics)	139
VIII-4	Second Breeding Period of *Trachelipus* Females Reared at Constant Temperatures	141
VIII-6	Percent Unsuccessful Broods in the First Period of *Trachelipus*, per Weight Class and Temperature*	141
VIII-7	Number of Days Needed by *Trachelipus* Females to Reach the Final Mean Weights (± S.D.) of Five Weights Classes[1]	143
VIII-8	Cumulative Total Mortality of Non-Breeding *Trachelipus*, in Percent of all Individuals Observed Through Each of the Four Weight Classes (Only the Lowest Class Includes Males and Females, in Unknown Proportions)	146
VIII-9	Percent Mortality Occurring Either During Gravidity or During the Post-Parturient Molt of Breeding *Trachelipus* Females	146
VIII-10	Summary of Board Collections of *Trachelipus* in 1978	147
VIII-11	Breeding Periodicity of *Trachelipus* Females in the Field, Categorized by Estimated Weights	154
IX-1	Mean Number of *Trachelipus rathkei* Per Board on Each Collection Date	160

TABLES

Number Page

X-1 Number of Days Needed for *T. rathkei* to Grow Through Each Weight Class at Three Temperatures. In Parentheses: Final Mean Weights ± S.E. 165

X-2 Percent Mortality, Within Four Weight Groups, of Non-Breeding *T. rathkei* Females at Three Constant Temperatures 167

X-3 Percent Mortality of *T. rathkei* Females Associated With Each Brood Within One Breeding Period (Three Consecutive Broods Occurred at 26.7°C Only). Assignment to Weight Classes is Based on Weights Just Prior to Each Brood 167

X-4 Degree-Day-Based Weight Class Durations for Breeding and Non-Breeding *T. rathkei* Females 169

X-5 Field-Collected Litter: Results of Analyses for Total Azinphosmethyl Residues, and Relationship of Collection Date to the Last Previous Spray Application Date 174

X-6 Cumulative Mortality Percentages for *T. rathkei* Reared on Contaminated Soil for 7 Days. Data Corrected for Control by Abbott's Formula. *) Indicates that the Values are Means Obtained From at Least 2 Replicate Runs (Containing 20 Animals Each) 175

X-7 Daily Mortality Records (Cumulated Percent) for II. Instar *T. rathkei* Reared on Azinphosmethyl-Contaminated Soil at Three Temperatures (20 Animals Per Pesticide Level and Temp) 176

X-8 Cumulative Percent Mortality, Over 6 Days, of *Trachelipus* of Various Weights Exposed to Field-Collected Litter Contaminated With Guthion (21°C Constant Temperature). (n = Total Number of Animals Per Run, Distributed as 2 Per Container) 178

X-9 Comparison of Field Data With Model Predictions. Columns 3 and 4 are the Ratios of Numbers of Pre-Reporductive (<12 mg) *T. rathkei* Collected Per Sampling Board From Control Plots to Number Per 5 Board From Sprayed Plots, for Each Sampling Day. Last Two Columns are the Model's Prediction, Given the Environmental and Pesticide Application Inputs Observed in the Field, of the Ratios of <12 mg and ≥ 12 mg Populations From Unsprayed and Sprayed Plots on the Same Day 191

Summary and Recommendations

A conceptual model was developed to describe aspects of the fate and effects of a pesticide in an orchard ecosystem. In order to refine, parameterize, and test a mathematical model based upon this conceptual model, a program of field and laboratory experiments was undertaken.

The environmental behavior of azinphosmethyl was studied in a Michigan apple orchard watershed to gather data for the model on initital distribution within the orchard, vertical movement of the pesticide under the influence of rainfall, loss from the orchard with runoff, and effects of the pesticide on several orchard invertebrate populations. The estimated proportion of a low-volume application initially distributed within the orchard averaged .624 (standard deviation of .149) over three seasons (1976-1978). Examination of residues reaching each layer showed the majority of the dislodgeable residues were distributed to the trees and grass-broadleaves. The litter-moss and soil contained residue levels roughly ten times lower than tree leaf residues. Runoff studies indicated loss, via this route, of less than 1% of azinphosmethyl residues present in the orchard. The residue data were used to parameterize a model for azinphosmethyl attenuation and movement in an orchard ecosystem. Rates of pesticide attenuation within, and movement between, specified orchard compartments were determined under various rainfall regimes. The output of this model was structured to allow the estimation of the time course of azinphosmethyl exposure to ground-dwelling invertebrates. Mean squared errors for the comparison of the model predictions with an independent set of residue data indicated good prediction of azinphosmethyl fate within the tree and grass-broadleaves layers. Prediction of pesticide dynamics within the litter-moss and soil layers was much more difficult. The model estimates that under dry conditions 25% of the daily loss of azinphosmethyl from the orchard trees is due to movement to other parts of the orchard. Greater movement is predicted under rainfall conditions. Estimates of daily airborne loss determined from deposit residues and direct sampling of airborne residues suggest that airborne loss is largely responsible for the early loss of residues, accounting for 40% of the daily loss rate on day 3 of the first spray period, 1978 season. A multi-component kinetic model is presented for estimating simultaneously the early airborne loss of foliar deposits and the often slower dissipation of the remaining residues. Further model development to include the effect of selected environmental parameters on azinphosmethyl degradation was also undertaken.

The generalized model developed, entitled the Pesticide Orchard Ecosystem Model (POEM), includes as a special case the model for the azinphosmethyl applications under the conditions of this field study. POEM also includes facilities for altering parameters to describe effects of other formulations, other pesticides, other application procedures and/or other field conditions.

The field sampling program for invertebrates included pit-trappping, block sampling for earthworms, and cryptozoan board sampling for isopods. Relative population densities in control plots versus plots sprayed with azinphosmethyl, followed in some cases by diazinon, were determined.

Laboratory cultures of the isopod Trachelipus rathkei and the collembolan Folsomia candida were established. Laboratory data were obtained to aid in parameterizing both life cycle models and azinphosmethyl toxicity models for populations of these organisms. Limited lab studies of azinphosmethyl toxicity to earthworms (Allolobophora caliginosa) and spiders (Lycosa lugubris) were also performed. The four models developed for invertebrates are components of the POEM model, and use daily predicted pesticide levels in various environmental compartments (e.g., grass/broadleaves, litter/moss, soil) to predict pesticide-induced mortality of the populations over long periods of time. The model, laboratory data, and field data for T. rathkei are presented in detail in this report. For the other organisms, the field and laboratory data are presented, but the models are described only in more general terms.

Two appendices describe (A) the procedure used to process the field data on pesticide residues to provide parameters for the fate portion of the POEM model, and (B) the Users' Manual, including sample output, for the POEM model.

Recommendations

(1) Further work to refine, parameterize, and test the components of the POEM model, or similar models, for other pesticides and other conditions should be undertaken. In many cases, the current froms are derived based on very sparse data in the literature. While predictions based on these forms may be very informative and useful in some contexts, they are not likely to be very accurate for predicting actual fate and impacts of pesticides until they have been carefully refined based on currently non-existent data. Nevertheless, the present model may be helpful because it allows the user to determine the implications of various sets of assumptions about pesticide dynamics and effects.

(2) Work on models for the long-term effects of pesticide exposure on populations of invertebrates should be continued. While this study includes a reasonable model for effects of azinphosmethyl on isopods and less refined models for collembola, earthworms, and spiders, the methodology should be extended and refined through application to other pesticides and organisms.

(3) The model presented here does not provide an overall indicator of the ecosystem-level impact of a pesticide in a particular situation. While impacts on individual populations are likely to be key components of any sound measure of overall impact, the importance and role of each population in the ecosystem must also be defined and incorporated in the measure. Research aimed at identifying key populations and modeling their functions should be undertaken. The search for integrating measures or indicators of ecosystem stress or damage for terrestrial systems should be broadened and intensified.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance and guidance of their project officers at the Environmental Research Laboratory in Corvallis, Dr. James Gillett and later Dr. Jay Gile. The contributions of many at M.S.U. are deeply appreciated. Jay Hestbeck, Mehrdad Tabatabai and Paul Weston, graduate students in Systems Science, contributed heavily to the modeling work. Programming was done by Tom Julien, Steve Walsh, and Mike Sayen. Chemical analyses, while directed by Drs. Kon, Jenkins and Zabik, involved many student laboratory assistants, whose contributions are appreciated. Roseann Miller and Kay Grimnes assisted in laboratory rearing of invertebrates.

The contributions of Drs. A. W. A. Brown, W. E. Cooper and J. W. Butcher, particularly to the early phases of the project, are gratefully acknowledged.

The authors are grateful the excellent contribution of Gwen Counseller and Julia Pond to the preparation of this report.

INTRODUCTION

Since the discontinued use of many organochlorine insecticides in the early seventies, use of the generally more toxic and less persistent organophosphate insecticides has increased (Brown, 1978). Because of the greater mammalian toxicity of these compounds (Matsumura, 1975), research of their fate in orchards has been primarily concerned with worker reentry hazard associated with foliar dislodgeable residues, soil, and soil dust residues. Most of this work has been done for citrus (Gunther et al., 1977; Nigg et al., 1977; Thompson and Brooks, 1976; Spear et al., 1978), but studies have also been conducted for peach (Winterlin et al., 1975; Hansen et al., 1978) and apple orchards (Staiff et al., 1975; Hansen et al., 1978). Little work has been done in the area of attenuation and movement of the organophosphates between trees, ground cover, and soil, or loss with runoff from deciduous fruit orchards.

The lack of cultivation, which is the practice in many deciduous fruit growing areas (Haynes, 1980), preserves greater species diversity than is found in many other agroecosystems (Brown, 1978). This diversity can result in a relatively stable deciduous tree fruit ecosystem if undisturbed by pesticides or other management practices (Hoyt and Burts, 1974). Under these conditions, natural control of many arthropod pests through disease, predation, and parasitism is achieved (Croft, 1975). However, to produce marketable fruit, pesticides must be used to control a few key pests (Glass and Lienk, 1971). Control of these key pests with pesticides may reduce natural enemy populations, promoting secondary pests to a major pest status, often requiring additional chemical control (Hoyt and Burts, 1974; Croft, 1978). In addition, the increased use of pesticides in orchards, and on all crops, has resulted in an increased number of resistant pest species (Smith, 1976; Brown, 1977, 1978; Croft, 1978). These and other problems associated with the use of pesticides as a sole means of control have resulted in a greater emphasis being placed on integrated pest management as a long-term strategy for the economic control of crop pests (NAS, 1969; Smith, 1976). Such programs are designed to use a broad spectrum of control measures including biological, cultural and chemical methods. This approach to pest management requires a great deal more knowledge not only of the ecobiology of both beneficial and harmful species, but also of pesticide fate and effects. The success of orchard IPM programs may depend largely on the judicious use of pesticides allowing maximum benefit to be gained from biological control measures (Croft and Brown, 1975; Smith, 1976). This will require a better understanding of pesticide fate throughout the entire orchard ecosystem.

Additional consideration must be given to species other than those of benefit to pest control. Because of their relative permanence, deciduous orchards are often a habitat for wildlife indigenous to natural ecosystems (Croft, 1978). Detailed studies of pesticide fate and effects, which would be impractical or undesirable in a natural setting, can be done in an orchard, to give some insight into the ecological hazards associated with pesticide exposure to the fauna of these environments. Such information may be valuable in the development of environmental fate and ecological effects testing guidelines as proposed under the Toxic Substance Control Act and the recently amended Federal Insecticide, Fungicide and Rodenticide Act.

The Toxic Substances Control Act authorizes the Environmental Protection Agency (EPA) to obtain from industry data on the production, use and effects on human health and the environment of chemical substances and mixtures. Testing standards under Section 4 are directed at specific chemical characteristics and effects, including oncogenicity, teratogenicity, mutagenicity, and other health effects, as well as environmental fate, persistence and ecological effects. All tests are substantially similar to methods proposed by EPA for its pesticide registration program and represent a "base set" of tests from which to select specific tests for specific chemicals in test rules. To date no test standards have been proposed for environmental fate or ecological effects.

In addition to the Section 4 standards which are designed to test specific chemicals or chemical groups, the EPA also plans to issue testing guidelines consistent with these testing standards, but more general in nature, encompassing a wider range of chemical substances and effects of concern to EPA. These guidelines will also be used under Section 5 which allows the agency to limit manufacturing, processing, distribution, use or disposal of new chemical substances (or new uses of existing substances), pending development of information. The administrator is given this authority if he has reason to believe (1) that the chemical substance may present an unreasonable risk or may result in substantial human exposure or environmental release, (2) there are insufficient data or experience for determining or predicting health or environmental effects, and (3) testing is necessary to develop such data. TSCA does not require EPA to provide testing guidance, except when specifically requested under Section 5 (g). Nevertheless, testing guidelines are presently being developed in an effort to streamline the monumental task of TSCA compliance and to encourage more appropriate and cost-efficient information gathering.

So far the EPA has proposed general standards for a number of human health effects. Such standards for environmental fate and ecological effects are presently at the interagency review stage. To develop generic standards for human health involves only one species, man. Types of exposure (dermal, inhalation, ingestion, etc.), metabolism, and pharmacodynamics are fairly uniform. Generic test standards may need only be modified based on the properties of the chemical or chemical category. Generic standards for environmental fate and ecological effects involves all species of flora and fauna. In addition, all biotic-abiotic relationships must be considered from ocean food chains to soil microbial communities. This diversity of species (and species interaction) and environments makes the development of generic standards to assess the possible hazards of chemical substances to the environment a formidable task. The first problem would seem to be how many different species must be tested to adequately assess ecosystem effect; secondly, what chemical properties are important, and, thirdly, what and how do environmental properties influence exposure and possible ecotoxicity. Due to the enormous complexity, there has been much controversy over the rationale for adopting standards in these areas where scientific methods are less developed and where no validated techniques are available for certain effects.

There may be unreasonable risk to an ecosystem when a component or components are exposed to a concentration of a chemical substance which causes harm. Environmental fate studies are used to predict and estimate the presence of potentially harmful chemical residues in man-made and natural environments. A chemical released into the environment may be transformed by chemical or photochemical reaction, be metabolized by living organisms or persist unaltered. Some degradation and transformation products can be hazardous in their own right (Menzie, 1972; Crosby, 1973; Goring et al., 1975). The goal of environmental test standards should be to identify the dominant pathways by which a chemical degrades, dissipates, and accumulates, and then relate this behavior to various chemical, physical, and biological conditions. This knowledge can then be used to infer what biota may be exposed to the chemical, by what route, how often, and in what concentrations. Thus, both the population at risk and the effect of the chemical are determined partly by the detailed fate of the chemical substance. Just as in health effects testing, where in vitro studies and lab animals are used to estimate chemical effects on man, ecosystem effects and chemical fate are estimated primarily from laboratory studies. The foundation for use of laboratory data for environmental fate assessment is based on the following assumptions:

(1) The rate of transformation or transport of a chemical in or from an environmental system is the sum of the rates of known individual chemical, physical, and biological processes and the rate of equilibrium constants for these processes can be predicted or measured independently in the laboratory.

(2) The laboratory data for individual processes can be integrated and extrapolated to the appropriate set of environmental conditions.

It is yet to be seen if any set of laboratory tests can be used to predict the environmental fate of a chemical substance to the extent that the EPA may adequately assess the possible risk to an ecosystem. The fact is that few of the processes which determine the environmental fate of a chemical substance have been studied in enough detail to predict dominant pathways or rates of change in the "real world." Each possible transformation or transport pathway can be studied in the laboratory and rates may be determined under a given set of "environmental conditions" but how actual environmental conditions influence rates is largely unknown.

A few years ago it was thought that microcosms, controlled laboratory systems that attempt to simulate some selected portion of the real world, might be used to fill this information gap. In a terrestrial microcosm environmental parameters such as temperature, light level, water content, and organism diversity can be controlled and varied by the investigator. A common approach to microcosm development has been to organize some elements of a selected ecosystem in a container so as to resemble some aspects of the ecosystem of interest and then systematically to change the complexity by adding new trophic levels of organisms. Parameters of the system as they affect chemical fate are monitored (Gillette and Witt, 1979). Unfortunately, development of the physical models of these microcosms has not always kept pace with conceptual development. More importantly, complete understanding of the discrete chemical, physical, biological, and climatological processes that control chemical fate in a terrestrial system is not yet directly obtainable from these studies.

Another approach has been to use mathematical models. The development and use of mathematical models usually involves a systems approach; the formalized analysis of any system or of the general properties of systems.

The analysis of complex systems as systems, and the modeling of these systems, is contrary to reductionist trends in science. Laboratory experiments which isolate and control very small components of nature have up to the present been the most powerful investigative tools aiding man in understanding nature, but this "science by isolation" has its drawbacks as the larger environment may influence the components of interest to such an extent that an isolated laboratory experiment may exclude some critical components, or the behavior of a system may not be simply the sum of the behaviors of its parts in isolation (Hall and Day, 1977). Mathematical modeling of environmental fate should be based on both reductionist laboratory experiments and key observations of the fate of chemicals in the environment to include the rates of transport and transformation as a function of climatic and other environmental variables. Only a handful of models have been developed which describe chemical environmental fate in general. The present "state of the art" model is EXAMS, a model of fate of toxic organic chemicals in aquatic ecosystems, developed by the EPA's Athens, Georgia Research Laboratory (Lassiter et al., 1978). This model was used to develop environmental assessments for eleven chemicals in aquatic systems based on laboratory measurements. The model has since been modified to include a library of canonical environments and is now in use on a trial basis in several laboratories and EPA offices.

The work presented here is one portion of an effort to characterize the dynamics and effects of an example compound in the terrestrial environment, utilizing primarily field measurements and the methodology of systems modeling and simulation. Data collection, model refinement, and revised experimental design were done iteratively, yielding a model which is parameterizable and data which are relevant to the problem being attacked.

The study of pesticide dynamics through *in situ* field studies is difficult due to the lack of natural or planned experiments (inability to control much of the variance, i.e., climatic conditions) and the relatively high levels of error associated with field data. Modeling techniques were employed to aid in the understanding of the necessarily large amount of field data needed to construct a "meaningful" picture of the pesticide's fate.

The field experimental program used to investigate the distribution, attenuation and movement of the organophosphate insecticide azinphosmethyl, 0,0-dimethyl-5-(4-oxo-1,2,3, benzotriazin-3(4H)-ylmethyl) phosphorodithioate (Guthion^R), in a Michigan apple orchard is given in Chapter I. The compound was followed from its spray application through the orchard vegetation/litter/soil environment and into aquatic systems. The form of the model describing azinphosmethyl movement and attenuation, as well as data handling procedures and the derived rates, are presented in Chapter II. Observations were made concurrently within the same orchard to examine the effects of azinphosmethyl on several ground-dwelling invertebrates, including detailed studies of the isopod *Trachelipus rathkei* (Snider, 1979; Snider and Shaddy, 1980). Field and laboratory data collected on *T. rathkei* were used to develop a model describing its ecobiology and temporally-distributed pesticide-induced mortality. The output of the fate model described in Chapter II was used to determine the time-course of azinphosmethyl exposure.

In Chapter III the field experimental program used to determine azinphosmethyl airborne residues is presented. A multi-component kinetic model used in the assessment of the contribution of airborne loss to the overall attenuation of deposit residues is also described.

In Chapter IV, movement and attenuation of azinphosmethyl are examined as a function of environmental conditions. A computer simulation is described which allows the user to predict the fate and effects of aziophosmethyl on several types of organisms.

Chapter V describes the results of the field sampling program for invertebrates in the orchard plots, providing information on the effects of aziophosmethyl spraying (additional material on the isopod *T. rathkei* is found in Chapter IX). Chapter VI contains the results of a laboratory assessment of the toxicity of asinphosmethyl and diazinon to various invertebrates. Chapter VII briefly describes the models developed for spiders, earthworms, and springtails. Chapter VIII presents a detailed description of the ecobiology of the isopod *Trachelipus rathkei*, while Chapter IX describes the effects of the aziophosmethyl spray program on the *T. rathkei* field population. Chapter X presents the model for *T rathkei*, including both its general life cycle and its response to pesticide exposure.

Appendix A documents the data analysis procedures employed locally at MSU to parameterize the model. Appendix B is the users' guide for the Pesticide Orchard Ecosystem Model (POEM) described in this report.

CHAPTER I

EXPERIMENTAL DATA FOR THE AZINPHOSMETHYL FATE MODEL

Reported here is the field experimental program used to investigate the distribution, attenuation, and movement of the organophosphate insecticide azinphosmethyl, 0,0-dimethyl-5(4-oxo-1,2,3, benzotriazin-3(4H)-ylmethyl) phosphorodithioate (Guthion^R), in a Michigan apple orchard. Studies were carried out to gather data on both initial distribution of azinphosmethyl within the orchard and vertical movement of the pesticide under the influence of rainfall, as well as the attenuation of the pesticide in various situations. In addition, plots were designed such that each was a separate watershed, allowing runoff collection from them individually. The compound was followed from its spray application through the orchard vegetation/litter soil environment and into aquatic systems, to determine possible exposure of the orchard ecosystem biota to the compound. The data presented here were used to parameterize a model (presented in Chapers II and IV) for azinphosmethyl attenuation and movement in an orchard ecosystem.

ANALYTICAL METHODS

Organic solvents were glass-distilled and the water was distilled-deionized. After washing, the glassware was rinsed with acetone and hexane followed by overnight heating at 250°C.

Dislodgeable Residues. Dislodgeable residues were determined by the procedure of Gunther et al. (1973). Leaf discs were extracted with 50 ml portions of water containing two drops of Triton X-100 in water (1:50,v/v). Samples were then agitated on a wrist-action shaker for 15 minutes. Depending on the bulkiness of the grass, litter, or moss, more water was used to insure good contact with the sample during extraction. One drop of Triton-X 100 solution was added for each additional 25 ml of water used. All samples were given a final rinse by hand with a third 50 ml portion of water. The combined washes were partitioned three times against 50 ml portions of hexane which was then concentrated on a rotary evaporator and diluted to a proper volume for analysis. Using the above method, recovery and standard deviation from the Triton-X 100 water solution fortified with azinphosmethyl standard was 95 ± 3%.

Surface-Penetrated Residues. To estimate the magnitude of the remaining residues on or within the cuticular matrix, selected samples collected on the day of application were given an additional extraction in a manner similar to that described by Steffens and Wieneke (1976). Three 20 ml volumes of acetone-water extracts were concentrated by rotary evaporation to remove the acetone. The water left in the rotary flask was partitioned in the flask against three 30 ml volumes of hexane which were combined and then dried over anhydrous sodium sulfate and concentrated to about one ml. This procedure was selected as Wieneke and Steffens (1974) were able to recover 100.4% of the ^{14}C azinphosmethyl applied to bean leaves as an aqueous formulation, one day following application.

This extract was cleaned up by the silica gel microcolumn described by Kadoum (1967) with our elution system. One and a half grams of unactivated Adsorbosil CAB, 100/140 mesh (Applied Sciences, Inc.) was packed as a hexane slurry into a Pasteur pipet. The sample was added in hexane and the column eluted with 15 ml of 10% benzene in hexane. Ethyl acetate (4%) in benzene then eluted the azinphosmethyl in 15 ml. Recovery and standard deviation of 2 ml of a 5 ppm azinphosmethyl standard solution added to the column was 94 ± 3%.

Soil. Extraction of soil was based on Schulz et al. (1970). Approximately 50 g of soil (largest roots removed) were mixed with 10 ml of water, if dry, and acetone (1.5 ml/g) on a wrist-action shaker for 15 minutes. The solvent was poured into a rotary flask through a funnel lined with Whatman No. 1 filter paper; as much soil as possible was retained in the extraction flask. A second extraction followed and the combined extracts were treated exactly as the surface-penetrated residues of the previous section, including the clean-up column. Recovery and standard deviation from soil fortified with azinphosmethyl standard was 84 ± 9%.

Filter Paper Targets. Targets, consisting of two circles of Whatman No. 1 paper, 18.5 cm in diameter (attached one atop the other, by a single staple to a cardboard backing), were extracted for two hours in a soxhlet extractor using a mixture of hexane:acetone, 100 ml:25 ml. Recovery and standard deviation from targets fortified with azinphosmethyl standard was 104 ± 5%.

Pesticide Runoff Studies. Azinphosmethyl in runoff samples collected during the 1977 season was examined by extracting one liter subsamples following centrifugation to remove sediment. The sediment was soxhlet extracted for four hours with a 1:1 hexane:acetone mixture, air dried and weighed. The supernatant was extracted with hexane and both sediment and supernatant extracted with hexane and both sediment and supernatant extracts were concentrated by rotary evaporation. Recovery and standard deviation from runoff water fortified with azinphosmethyl standard was 93 ± 4%.

Quantitation of azinphosmethyl was accomplished using a Tracor 560 gas chromatograph having a flame photometric detector in the phosphorus mode. A six-foot glass column (2 mm i.d.) packed with 3% SE-30 on Gas Chrom Q,60/80 mesh, was operated at 195 C; N_2, 40 ml/min; air, 90 ml/min; H_2, 60 ml/min. This system was interfaced with a Digital PDP 8 Pamila PDP 11/40 RSTS computer for integration of the area under the single peak produced.

THE EXPERIMENTAL SITE

The experimental apple orchard was located in the vicinity of Grand Rapids, Michigan in Kent County. The twelve-year old trees were a mixture of semi-dwarf duchess and wealthy cultivars. In 1976 the orchard had been left unattended for approximately five years. This was a necessary requirement to assure adequate populations of ground-dwelling invertebrates, unaffected by previous seasons' pesticide applications (Snider, 1979). In the early spring the trees were pruned and understory brush was removed. Just prior to the first spray application the area was mowed to a height of approximately five cm. Due to dry conditions further mowing was not necessary. In 1977 light pruning was repeated and the orchard was mowed just prior to the first, second, and fourth spray applications. A survey of the ground cover by the line-transect method (Cox, 1974) was carried out in 1976; cover type categories were established and their importance values calculated. Above the soil (a marlette sandy clay loam, pH 6.0, 56% sand, 20% silt, 24% clay, and 6.0% o.m. in top 10 cm) was moss intermingled with litter; the most recent litter deposits covered the moss. The herbaceous growth covering the moss and litter was predominantly broad-leaved weeds, with grass being of secondary importance. An examination of the ground cover in the areas sampled for residue analysis yielded similar results. This ground cover composition is not atypical of orchards in the temperate Eastern United States and Canada, although they vary with the level of secondary succession (Whittaker, 1975), climatic, topographic, edaphic conditions, and management practices (Klingman and Ashton, 1975; Teskey and Shoemaker, 1978; Schubert, 1972).

PREPARATION OF ORCHARD FOR RUNOFF COLLECTION

To facilitate the study of azinphosmethyl loss via runoff, four experimental plots and one control plot were established, each a separate watershed (Figure I-1). Slopes in plots 1 and 2 and the control were between 6 and 12%, slopes in plots 3 and 4 were between 18 and 25%. All the runoff was collected from a given plot for each event and subsampled for pesticide analysis. A 600-liter galvanized steel livestock tank (61 cm x 61 cm x 183 cm) was placed in an excavation at the natural drainage point for each plot, at a level to collect the runoff. A smaller tank (40 liter capacity) was placed inside the larger tank so that it would fill and any overflow would be contained in the larger tank. Also, an overflow diversion pipe was installed on the collection tank for plot 1; in the event the large tank overflowed, the runoff water would be diverted to a point below plot 4 (see Figure I-1). Runoff water was finally channeled into the tanks by galvanized steel collection chutes, 61 cm long with sides 15 cm high, 61 cm wide at the top and 30.5 cm wide at the bottom. A 61 cm by 61 cm area of the tank directly below the chute was covered with a 6.4 mm mesh screen and the rest of the tank was covered with plywood covered with plastic, to keep out rainfall, animals, and debris. The chute and screen were also covered with plastic. Both the tanks and chutes were coated with epoxy paint, as tests showed that after seven days, the residues remaining from a five ppb solution of azinphosmethyl in galvanized steel containers were 30% less than the residues remaining in glass, stainless steel, or epoxy-painted containers. Azinphosmethyl hydrolysis experiments (see Part IV) indicated little degradation over the seven-day period, at solution pH values below 7.0 (first order rate constant of .008 at 25°C). As the pH of the runoff water collected averaged 5.9 ± 0.2, losses by this mechanism prior to sample collection and extraction were thought to be small. Loss via volatilization was also considered to be negligible as azinphosmethyl has a vapor pressure $< 7.5 \times 10^{-6}$ mm Hg at 20°C (Mobay Chemical Co., personal communication) and the maximum concentration of azinphosmethyl measured in the runoff collected was 22 ppb, well below its water solubility of 33 ppm.

Plots were enclosed and separated from one another by a 30.5 cm, 20 gauge aluminum core fence buried approximately five cm in the ground. This fence was made continuous with the collection chute to aid in the final channeling of runoff at the bottom of the plot slope. Fencing was installed with minimal disturbance of the ground cover and in such a manner that potential runoff would have as little contact as possible with the fencing. This collection scheme was designed and implemented during the 1976 season, but due to dry conditions, no runoff was collected that year.

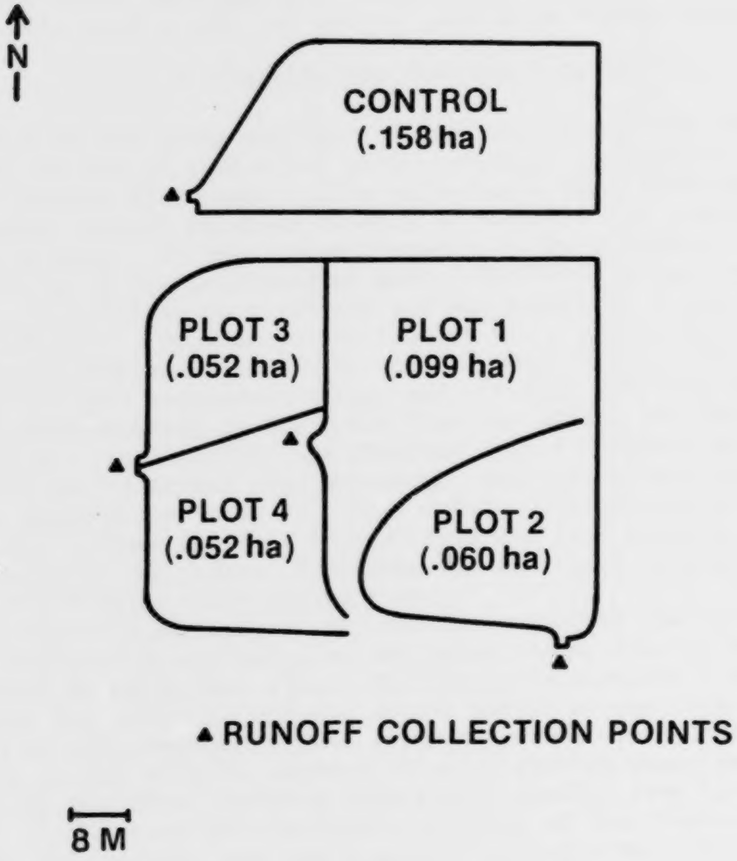

N
CONTROL
(.158 ha)
PLOT 3
(.052 ha)
PLOT 1
(.099 ha)
PLOT 4
(.052 ha)
PLOT 2
(.060 ha)
▲ RUNOFF COLLECTION POINTS
8 M

Figure 1-1. Orchard Plots

SPATIAL STRUCTURE OF THE ORCHARD PLOTS

The orchard plots (Figure I-1) were subdivided both vertically and horizontally in order to represent adequately the variations which affect the behavior and impact of the pesticide in the orchard ecosystem.

Horizontally, each plot was subdivided into four regions potentially different with respect to inital pesticide distribution (see Figure I-2). Vertically, each alley region was divided into three compartments: grass-broadleaves, litter-moss, and soil. The canopy regions contained these compartments plus a compartment for the leaves of the tree.

Region 4 (under the canopy) was determined to be 32% of the area in plot 1, 34% in plot 2, 54% in plot 3, and 45% in plot 4. The remainder of the plot area was divided among the three alley regions in a ratio of 2:3:1 for plots 1 and 2, and 1:2:1 for plots 3 and 4. The difference in the ratios was due to the closer spacing of the rows along the North-South axis in plots 3 and 4. The number of trees in each of the plots was as follows: plot 1, 24; plot 2, 15; plot 3, 10; and plot 4, 11. Tree heights average 3.0 meters.

SPRAYING AND SAMPLING SCHEDULE

The size of the plots and their inaccessibility due to the aluminum fences made the use of commerical spray equipment impossible. What was needed was a plot sprayer that could: 1) be pulled by a small tractor, such as a garden tractor, and 2) match as closely as possible the coverage of a commercial spray unit. To meet these criteria, a low pressure, low volume sprayer similar to one developed by Howitt and Pshea (1965) was constructed. The sprayer was mounted on a trailer and was pulled by a John Deere model 200 garden tractor. Mounted on the trailer was a double inlet, high volume, low velocity blower manufactured by Dayton, model 3C011. The blower was powered by an eight horsepower Briggs and Stratton gasoline engine. Blower output was approximately 10,000 cubic feet per minute (at the highest engine speed setting). The air flow was directed by a fiberglass deflector, constructed for use on Agtech crop sprayers. One side of the deflector was widened to accommodate three Beecomist model 350 mini-spin spray heads. The deflector was further modified between 1976 and 1977 seasons to direct more of the spray into the trees. Pesticide was delivered to the spray heads by a Masterflex variable speed tubing pump.

The pesticide application rate was determined by the rate at which the pesticide mixture was delivered to the spray heads, tractor speed, and distance covered to spray each plot. The actual application time was recorded in the field for each plot and the actual amount of pesticide applied was determined by tank residual volume after spraying. In addition, during the first spray period of 1978, samples of spray mixture were taken, at the spray heads, before and after spraying each plot. Results from this method were comparable to those of the comparable to those of the residual volume method. The average application rate and standard deviation was 1.62 ± .33 kg/ha 50% w.p./100ℓ/ha in 1976 and 1.64 ± .38 kg/ha 50% w.p./100ℓ/ha in 1977. Plots were sprayed in sequence between 7 a.m. and 9 a.m.

Deposit Residue Samples

To determine initial horizontal distribution of azinphosmethyl, a series of 15 to 20 ground-located filter paper targets was deployed among the four horizontal regions (see Figure I-2) in each plot on the date of spraying.

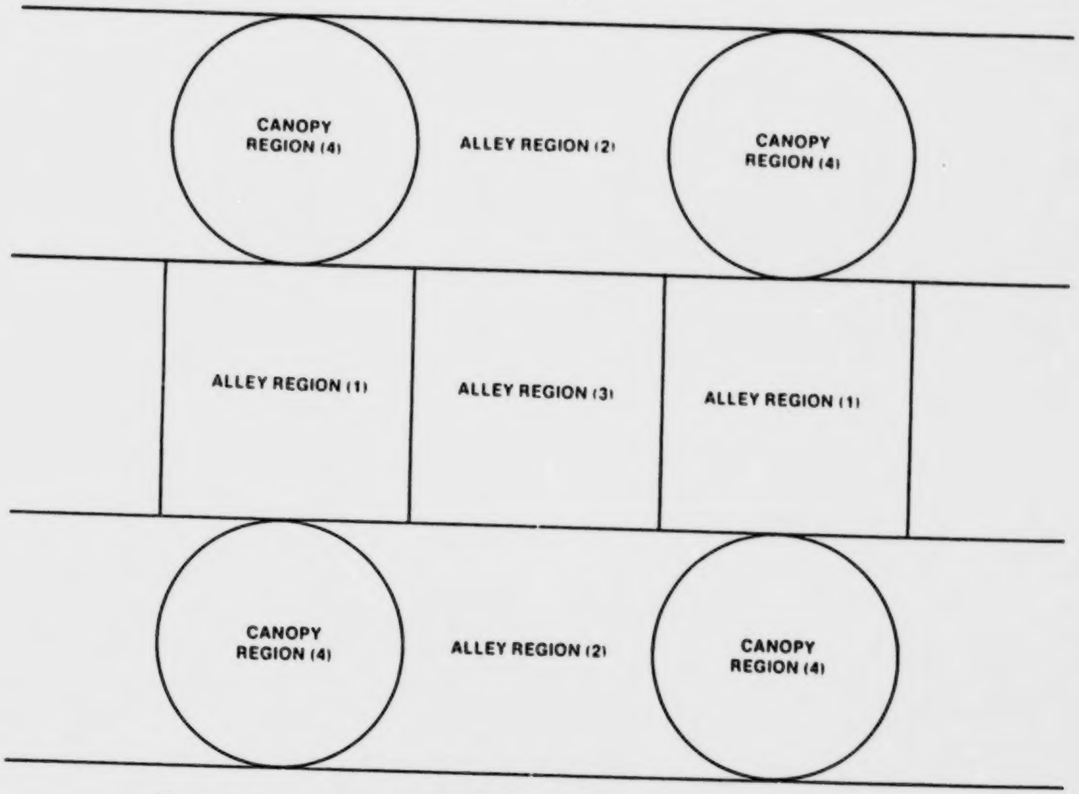

CANOPY REGION (4)
ALLEY REGION (2)
CANOPY REGION (4)
ALLEY REGION (1)
ALLEY REGION (3)
ALLEY REGION (1)
CANOPY REGION (4)
ALLEY REGION (2)
CANOPY REGION (4)

Figure I-2. Overhead View of Horizontal Regions of Orchard Plots

Targets were placed in the center of the alley regions, and at the in-row midpoint between the tree trunk and the edge of the canopy region. As soon as a plot had been sprayed, the filter papers were removed from the backing, packaged, and transported in picnic coolers cooled by dry ice. Storage was at -20°C until analysis.

The initial distribution of azinphosmethyl was also determined among the three ground layers: grass-broadleaves, litter-moss, and soil. In each plot, two samples of each layer were taken from the tree and alley regions. A square of sod (15 cm x 15 cm) was cut to a depth of about four cm and the grass-broadleaf plants, litter, and moss were separated into three discrete samples for residue analysis. From the bare sod remaining, three cores (5 cm x 7 cm deep) were taken for analysis providing a sample of 40 to 60 g.

For analysis of leaf deposits a 2.0 cm diameter disc was taken from the center of each leaf. Three trees were sampled in each plot, taking 30 or more discs per tree. Samples were taken at shoulder height (distributed within the canopy easily reached) around the entire circumference of the tree.

Sampling dates for the 1976 season are shown in Table I-1. Infrequent rainfall during this season yielded little information usable to assess movement due to rainfall. In 1977, interspray sampling was optimized for movement data as samples were collected primarily after rainfall events (see Table I-2).

Residues in Runoff

Azinphosmethyl movement out of the orchard with runoff was also determined. Runoff water was removed from the orchard in four-liter, dark glass bottles and stored at 5°C until analysis. Excess runoff was measured volumetrically in the field and discarded.

Rainfall was measured with static rain gauges and this information was correlated with data from recording rain gauges maintained 3/4 mile from the orchard by the Michigan State University Institute of Water Research. Temperature and humidity data shown in Figures I-5, I-6, I-7 and I-8 were obtained from the Michigan Weather Service, Grand Rapids, Michigan.

RESULTS AND DISCUSSION

Initial Horizontal Distribution

Table I-3 and I-4 show the results of the analysis of the filter paper targets for the first spray day of the 1976 and 1977 seasons. The average amount and standard error (SE) of pesticide are expressed in $\mu g/cm^2$ ground area and proportions shown are proportions of dose applied. The grand average across plots 1 through 4 for both seasons shows that alley region 2 and the canopy region received the majority of the residues reaching the ground; alley regions 1 and 3 received less. Pesticide distribution was more uniform in the 1977 season, and residue levels were proportionally lower across all regions. The authors believe this was due to modification of the sprayer between seasons, after which more of the spray was directed into the atmosphere and away from the ground.

Initial Vertical Distribution

Azinphosmethyl initial vertical distribution for the 1976 and 1977 seasons is given in Table I-5. Each plot is represented by only two regions; alley and canopy. In 1976 the alley was randomly sampled. In 1977 the average

TABLE I-1. SUMMARY OF SIGNIFICANT EVENTS FOR THE ORCHARD, 1976 SEASON

Spray Date	Sample Date	Rainfall Date	Rainfall Amount		Days Since Spray
			mm	in	
		Orchard Mowed 28 June			
		30 June	36.3	1.40	
2 July	2 July				0
	6 July				4
	9 July				7
	14 July				12
15 July	15 July				0
	20 July				5
		20 July[a]	22.9	.90	
	22 July				7
		26 July	06.4	0.25	
	27 July				12
28 July		28 July[b]	11.4	0.45	0
	29 July				1
		31 July	04.6	.18	
	2 August				5
	4 August				7
		5 August	10.2	.40	
	10 August				13
		14 August	27.9	1.10	
	16 August				19
17 August	17 August				0
	20 August				3
	24 August				7
		28 August	06.4	0.25	
	30 August				13

[a] Rainfall started immediately after spraying.

[b] Rainfall occurred after sampling.

TABLE I-2. SUMMARY OF SIGNIFICANT EVENTS FOR THE ORCHARD, 1977 SEASON

Spray Date	Sample Date	Rainfall Date	Rainfall Amount mm	Rainfall Amount in	Days Since Spray
		Orchard Mowed 23 May			
		25 May	5.1	0.20	
26 May	26 May				0
		39 May	20.3	0.80	4
	1 June				6
		4 June	25.4	1.00	10
	6 June				11
		11 June and 12 June	12.7	0.50	17
	13 June				18
		Orchard Mowed 15 June			
16 June	16 June				0
		17 June and 18 June	6.4	0.25	2
	20 June				4
		27 June	5.1	0.20	11
	28 June				12
		30 June	25.4	1.00	14
	1 July				15
		4 July	12.7	0.50	20
		7 July[a]	5.1	0.20	22
7 July	7 July				0
		18 July	22.9	0.90	11
	19 July				12
		Orchard Mowed 20 July			
22 July	22 July				0
		24 July	2.5	0.10	2
	25 July				3
		29 July	2.5	-.10	6
	1 August				10
		3 August	2.8	0.11	11
		4 August	13.7	0.54	13
		6 August	3.8	0.15	15
	7 August				16
		8 August	2.5	0.10	17
		10 August	22.9	.90	
12 August	12 August				0
		13 August	12.7	0.50	1
	15 August				3
	18 August				6

[a] Rainfall occurred just prior to spraying.

TABLE I-3. AZINPHOSMETHYL INITIAL HORIZONTAL DISTRIBUTION FROM THE ANALYSIS OF TARGETS, 1976 SEASON

Plot		Alley(1)	Alley(2)	Alley(3)	Canopy(4)
1	Average Amount (μg/cm^2 ± SE)[b]	2.48 ± 0.22	3.35 ± 0.45	2.76 ± 0.34	2.89 ± 0.51
	Sample size	10	14	7	13
	Proportion[a]	.071	.131	.026	.093
2	Average Amount (μg/cm^2 ± SE)	1.36 ± 0.31	2.46 ± 0.44	1.65 ± 0.39	3.20 ± 0.37
	Sample Size	9	6	9	11
	Proportion[a]	.050	.079	.026	.136
3	Average Amount (μg/cm^2 ± SE)	.75 ± 0.20	3.81 ± 1.00	1.36 ± 0.50	5.10 ± 0.77
	Sample Size	5	5	5	7
	Proportion[a]	.009	.076	.023	.226
4	Average Amount (μg/cm^2 ± SE)	2.51 ± 0.95	3.06 ± 1.28	2.14 + 0.65	2.90 ± 1.10
	Sample Size	9	4	3	10
	Proportion[a]	.042	.111	.065	.175
Grand Average Amount (μg/cm^2 ± SE)		1.78 ± 0.44	3.7 ± 0.28	1.98 ± 0.31	3.52 ± 0.53

[a] Proportion of amount applied

[b] Standard error

TABLE I-4. AZINPHOSMETHYL INITIAL HORIZONTAL DISTRIBUTION FROM THE ANALYSIS OF TARGETS, 1977 SEASON

Plot		Alley (1)	Alley (2)	Alley (3)	Canopy (4)
1	Average Amount ($\mu g/cm^2$ ± SE)[b]	2.75 ± 0.63	3.12 ± 0.77	2.63 ± 0.50	3.55 ± 1.14
	Sample size	7	7	13	6
	Proportion[a]	.070	.114	.023	.095
2	Average Amount ($\mu g/cm^2$ ± SE)	1.34 ± 0.24	1.96 ± 0.12	1.24 + 0.26	1.83 + 0.44
	Sample Size	9	3	6	4
	Proportion[a]	.047	.109	.026	.103
3	Average Amount ($\mu g/cm^2$ ± SE)	1.03 ± 0.22	2.51 ± 0.13	1.34 ± 0.28	1.39 ± 0.45
	Sample Size	7	5	8	6
	Proportion[a]	.105	.064	.020	.088
4	Average Amount ($\mu g/cm^2$ ± SE)	.91 ± 0.43	2.27 ± 0.43	.978 ± 0.28	1.43 ± 0.09
	Sample Size	3	5	8	3
	Proportion[a]	.017	.079	.024	.093
Grand Average Amount ($\mu g/cm^2$ ± SE)		1.51 ± 0.42	2.47 ± 0.25	1.55 ± 0.37	2.05 ± 0.51

[a] Proportion of amount applied

[b] Standard error

TABLE I-5. INITIAL VERTICAL DISTRIBUTION OF AZINPHOSMETHYL DISLODGEABLE RESIDUES ($\mu g/cm^2$ ± SE)

Year		Tree	Grass-Broadleaves	Litter-Moss	Soil
1976	Canopy				
	Average Amount	2.92 ± .41	1.49 ± .40	.18 ± .04	.20 ± .05
	Sample Size	11	9	9	8
	Alley				
	Average Amount		1.72 ± .33	.15 ± .08	.19 ± .02
	Sample Size		8	5	8
1977	Canopy				
	Average Amount	2.88 ± .42	.55 ± .04	.29 ± .04	.29
	Sample Size	12	6	8	1
	Alley				
	Average Amount		1.15 ± .23	.27 ± .05	
	Sample Size		8	8	

[a] Soil residues were determined on a whole basis, value represents $\mu g/cm^2$ in the top 10 cm.

amounts for the alley represent weighted averages of alley regions 1, 2, and 3, weighted by percent of plot area. These data indicated that for both years the majority of the dislodgeable pesticide residues deposited in the orchard was initially distributed vertically to the tree and the grass-broadleaf layer. Azinphosmethyl residues distributed to the litter-moss layer and soil were roughly ten times lower than leaf residues.

Using the vertical distribution of the dislodgeable residue data along with the pesticide application rates and the plot characteristics, the proportion of the applied pesticide reaching each of the vertical regions was calculated on a plot basis and then averaged across plots (see Table I-6). To determine the amount of pesticide distributed to the tree leaves, the tree leaf surface area was estimated by removing all the leaves from two trees, one in plot 2 and one in plot 4, following the 1978 sampling season (an exhaustive search for other methods of determining tree leaf surface was unsuccessful). The leaves from each tree were contained in six 50 1 bags. Each bag was weighted and sub samples of ten leaves were randomly selected for each 500 g of leaves. Weights and areas were determined for each sub sample. Total leaf area was determined from these measurements and the total leaf weight. The average for these two trees was approximately 400,000 cm^2 (one side of leaf only). This is a crude estimate due to sampling limitations and is specific for the tree size and vigor found in this orchard. As the pesticide was not evenly distributed vertically in the tree, estimates based on leaf residue data taken from the lower half of the tree in the 1976 and 1977 seasons would tend to overestimate the proportion distributed to the entire tree. In 1978, the upper half of the tree was sampled separately. From these data, a ratio was determined by dividing the average amount of dislodgeable residue found in the entire tree (upper and lower) by the average amount of dislodgeable residue found in the lower half of the tree. This ratio was determined using an across-plot average for each of the sample dates for the first spray period of the 1978 season. A least squares linear regression of these ratios with time gave an intercept of .7027 and slope of -.0063T, T being the time since spray in days (r^2 = .836). The value for the intercept was then multiplied by the average lower leaf values for the 1976 and 1977 seasons to arrive at an estimate of the average leaf residue level for the entire tree (data in Table I-6 and Figures I-3 and I-4 have been adjusted accordingly). Due to pre-1977 sprayer design the 1976 data are probably still slightly overestimated. This estimate was then multiplied by 400,000 cm^2/tree and by the number of trees per plot. The result was divided by the leaves. The proportion of pesticide distributed to the tree included residues deposited on both leaves and bark. The proportion distributed to the bark was estimated at 15% of that going to leaves, based on the work of Steiner (1969).

The proportion of the pesticide applied that is distributed as surface-penetrated residues was estimated from matched samples from the first spray of the 1978 season. The surface-penetrated to dislodgeable residue ratios and standard errors were as follows; leaves, .081 ± .015; grass, .190 ± .002; litter, .421 ± .018; moss, .272 (one sample). These ratios were multiplied by the appropriate dislodgeable residue proportions to estimate the surface-penetrated residue proportion. All soil residues were determined on a whole sample basis. To estimate the amount of pesticide deposited in the orchard during spray application, all the dislodgeable, surface-penetrated and soil residue proportions were summed across both the alley and canopy regions. In 1976, 66.8% (SE .093) of the pesticide applied was estimated to be initially deposited to the various orchard layers. Confidence in this conservative

Table I-6. Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied (±SE), from the Analysis of Samples[a]

	1976				
	Alley		Canopy		
	Dislodgeable	Surface-Penetrated	Dislodgeable	Surface-Penetrated	Total
Tree[b]			.376 ± 082	.027	
Grass	.112 ± .015	.021	.060 ± .014	.011	.661 ± .093
Litter-Moss	.014 ± .005	.006	.013 ± .004	.033	
Soil[c]	.015 ± .002		.010 ± .006		
	1977				
Tree[b]			.337 ± .020	.022	
Grass	.070 ± .016	.013	.033 ± .009	.005	.556 ± .011
Litter-Moss	.018 ± .002	.007	.014 ± .004	.005	
Soil[c]	.015[d]		.015		

[a] Data averaged across plots for the first application of the season.

[b] The proportion distributed to the tree includes both leaves and bark.

[c] Soils residues were determined on a whole sample basis.

[d] 1976 value used as there are insufficent data for 1977.

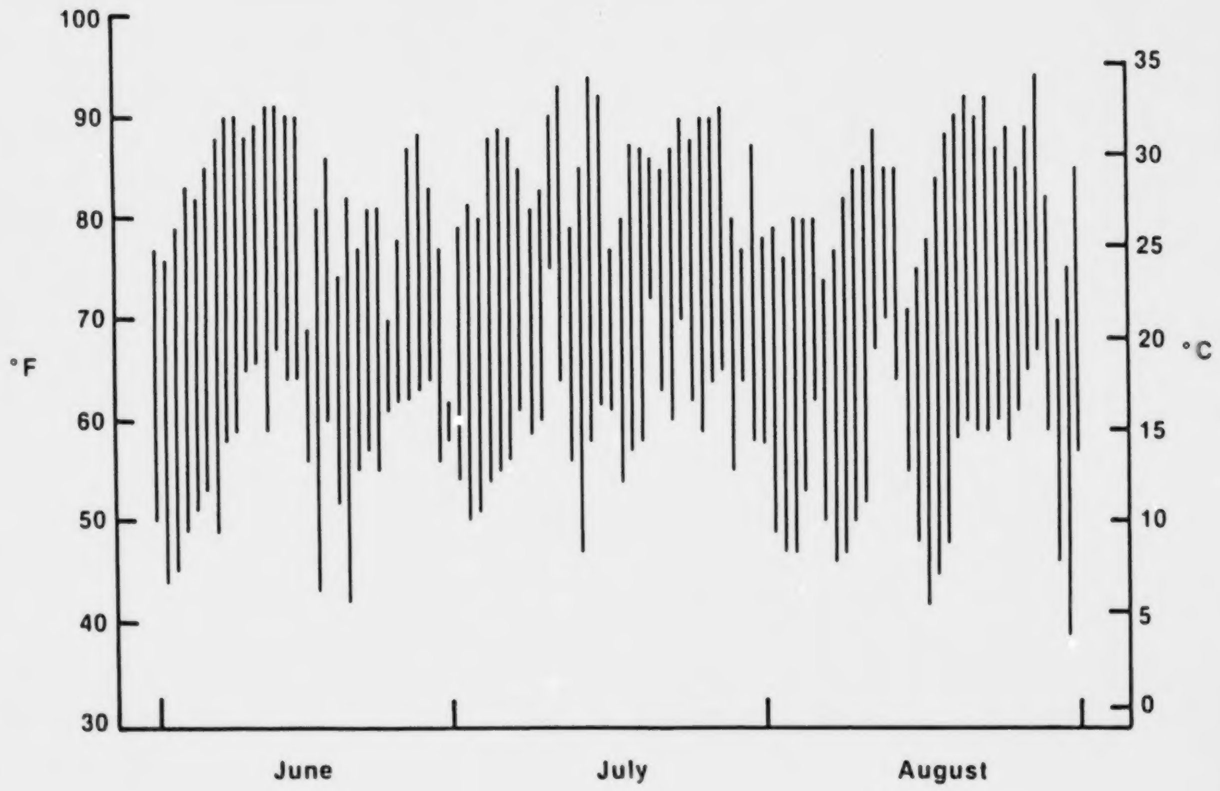


Figure I-5. Daily Temperature Range, 1976 Season

estimate is subject to the following sources of error; accuracy of amount applied, homogeneity of application, representative sampling of residue distribution, and the tree surface area estimate. The 33.2% not accounted for is assumed to be due to airborne loss, primarily as drift at application, but also as volatilization and wind erosion in the four hours between application and sampling. Another possible pathway of residues not accounted for is foliar penetration and subsequent unavailability to surface strip extraction. Numerous studies have compared dislodgeable to whole-leaf tissue residues (Winterlin et al., 1975; Elliot et al., 1977; Gunther et al., 1977). Their applicability to the present study is uncertain, as the degree of pesticide leaf uptake may vary with pesticide, formulation, mode of application, amount applied, leaf type, and environmental conditions (Hull, 1970). The efficiency of the solvent strip procedure used here, as compared to whole-leaf extraction procedures, in removing freshly deposited azinphosmethyl residues is not known. Use of the solvent strip procedure was based on the results of a detailed study conducted by Wieneke and Steffens (1974). These researchers found that 100.4% of the ^{14}C azinphosmethyl applied to bean leaves in an aqueous formulation could be recovered with a water followed by a benzene strip, for samples taken one day following application. In 1977 only 55.4% (SE .001) was estimated to be deposited in the orchard with 45.6% as airborne loss. A similar pesticide mass balance shown in Table I-7 uses the target data to estimate the proportion of the pesticide applied that reaches the orchard floor. Tree proportions were estimated in the same manner as for Table I-6. This treatment of the data shows that 74.1% (SE .099) of pesticide applied in 1976 was deposited in the orchard, on the average, with 25.9% as airborne loss. In 1977 61.0% (SE .034) was estimated to be deposited in the orchard with 39.0% as airborne loss. Analysis of the plot totals (Table I-7) using targets to estimate the proportion of the applied dose distributed to the orchard floor suggests that the amount remaining in the orchard following application is greater in 1976 than in 1977 (paired t-test of plot total proportions gave a $P<.15$). A similar analysis indicate that this difference was not due to amounts distributed to the trees but rather that proportion distributed to the orchard floor. The authors believe that this difference may be due to the between-season sprayer modification that directed more of the spray upward into the atmosphere and away from the ground. Wind speed and atmospheric stability during application may also have contributed to this difference. There is also some evidence that target residues as a proportion of dose applied were greater than the combined residues distributed to the various orchard floor layers (paired t-test of plot averages across both years gave a $P<.15$). As these data were normalized for extraction efficiency, this result would indicate a substantial loss in residues during the approximately four hours between spray application and sampling. The most likely sources of this loss are thought to be volatilization and/or wind erosion (Gunther and Blinn, 1955; Taylor et al., 1977).

Losses in Runoff

Azinphosmethyl levels found in runoff collected during the 1977 season are given in Table I-8. No runoff was found in the orchard plots as a result of the rainfall events that occurred on June 27, July 5, 7, 24, 28, and August 2, 4 (Table I-2). These rainfall events averaged 5.8 ± 3.5 mm (intensity, 2.6 ± 1.2 mm/hr) which is considerably lower than the average runoff-producing rainfall event of 21.2 ± 4.7 mm (intensity, 6.5 ± 1.8 mm/hr) shown in Table I-8. Rainfall events that occurred on June 11-12 and 17-18 produce

Table I-7. Initial Vertical Pesticide Distribution, as a Proportion of the Amount Applied, using Target Data to Calcualte Proportion Reaching the Orchard Floor

Plot	1976				
	Orchard Floor		Tree		
	Alley	Canopy	Dislodgeable	Surface-Penetrated	Total
1	.228	.093	.428	.030	.780
2	.155	.138	.374	.026	.694
3	.156	.181	.155	.011	.506
4	.218	.178	.547	.039	.985
					.741 ± .099
	1977				
1	.207	.096	.291	.021	.615
2	.182	.105	.387	.028	.702
3	.088	.101	.337	.024	.550
4	.120	.094	.334	.024	.572
					.610 ± .034

Table I-8. Azinphosmethyl in Runoff, 1977 Season

Date	Days Since Spray	Rainfall mm	Rainfall mm/Hr.	Runoff	Plot 1	Plot 2	Plot 3	Plot 4	Plot Control
30 May	4	20.3	5.1	mm x 10^{-2}	0.80	5.00	0.60	1.00	a
				Liters	6.0	20.0	3.5	4.0	
				PPb[c]	10.50	0.70	21.70	18.80	
4,5 June	10	25.4	9.8	mm x 10^{-2}	2.00	2.50	6.70	10.00	1.00
				Liters	14.0	9.8	40.0	40.0	20.4
				PPb	0.74	0.08	0.26	0.25	0.03
30 June	14	25.4	5.4	mm x 10^{-2}	1.00	5.60	1.70	0.10	a
				Liters	8.0	22.5	10.0	0.5	
				PPb	0.40	0.03	0.24	0.73	
18 July	11	22.9	7.1	mm x 10^{-2}	1.30	5.50	2.20	1.00	0.70
				Liters	10.7	22.0	13.0	4.0	10.0
				PPb	3.90	0.15	4.10	2.25	0.20
3,4,6 August	13	20.3	5.1	mm x 10^{-2}	0.06	2.60	0.50	3.10	a
				Liters	0.5	10.5	3.0	12.5	
				PPb	b	1.30	3.40	b	
13 August	1	12.7	6.4	mm x 10^{-2}	0.50	0.80	a	a	a
				Liters	4.0	3.0			
				PPb	14.35	b			

[a] No runoff collected.

[b] Runoff not analyzed.

[c] PPb of Azinphosmethyl in runoff water.

small amounts of runoff in some of the plots, but samples were not analyzed. Rainfall intensity for these two events was similar to those that produced no runoff but the duration of rainfall was slightly longer. The 25.4 mm (intensity, 8.4 mm/hr) rainfall that occurred on August 8-10 produced runoff in all but plot 4, but no analysis was undertaken as samples were not collected until after the spray application on August 12. No runoff-producing events occurred during the 1976 season. The concentration of azinphosmethyl in the sediment (sediment amounts were less than 0.5 grams per liter of runoff) was very small compared to levels in the water, and these data are not reported here. The lack of sediment is to be expected as the dense ground cover on the orchard floor allows little soil erosion (Asmussen et al., 1977; Harrold et al., 1970). The amount of runoff is also expected to be less than might be found from tilled fields of similar slope characteristics. This may be attributed to effect of ground cover, which increases infiltration and slows overland flow, thus decreasing total runoff and loss of pesticide. Many researchers have reported that concentrations of pesticides in runoff are highest for rainfall events occurring soon after application (Hall et al., 1972; Bauer et al., 1972; Glass and Edwards, 1974; Ritter et al., 1974; Caro et al., 1974). This is indeed what was observed for the pesticide levels in runoff for the orchard studied. The levels of azinphosmethyl in runoff collected on June 6, 10 days after application, were 10 to 100 times less than the levels found in runoff collected on June 1, just 4 days after application. Time since spray has an effect on the amount of pesticide in runoff only as it is related to the amounts of pesticide residue available to runoff. The amount of rainfall preceding the rainfall event that produces runoff also influences the amount of pesticide that is lost to runoff. A comparison of azinphosmethyl concentrations in runoff collected from plots 1, 3, and 4 on June 6 (10 days following application) with azinphosmethyl concentrations in runoff from the same plots collected July 19 (11 days following application) shows much higher levels in the July 19 runoff. This may be explained by the fact that although both events occurred approximately the same number of days following application, no rainfall occurred between application and the event producing runoff on July 19, whereas 20.3 mm of rainfall occurred just 4 days prior to the June 6 event. The intervening rainfall event not only produced runoff, removing pesticide residues from the orchard, but also redistributed those residues remaining such that they would be less likely to be removed with successive runoff. The fact that tree leaf residues for June 6 averaged .399, 1.267, and 1.225 $\mu g/cm^2$ for plots 1, 3, and 4, respectively, and leaf residues found on July 19 averaged 1.942, 2.286, and 2.374 $\mu g/cm^2$ for plots 1, 3, and 4, respectively, supports this hypothesis. In general, increased runoff caused increased pesticide loss so that the concentration of pesticide in varying amounts of runoff on a given day remained relatively constant. The data, for the most part, reflected this relationship, except for plot 2. Plot 2 was characterized by consistently high runoff compared to the other plots, but upon analysis, azinphosmethyl levels detected were considerably lower than those in the other plots. We have not yet arrived at a satisfactory explanation for this. One might hypothesize that collected runoff was coming from outside the plot or possibly was interflow from upslope that surfaced just prior to the collection point.

Overall it appears that the contribution of runoff to the azinphosmethyl loss from the orchard was quite small. For example, the 20.3 mm of rain on May 30 produced only .01 mm of runoff from plot 4, which contained 75 mg of azinphosmethyl, whereas 44 g were applied just four days prior to the event. This loss was well under 1% of the residues present at the time of the rainfall.

Residue Data

Figures I-3 and I-4 represent azinphosmethyl dislodgeable residues for the various above ground layers and soil residues, for alley and canopy regions. Leaf residues are shown as entire tree estimates using the method described for Table I-6. Prior to averaging across plots, statistical outliers were determined and eliminated using the test proposed by Grubbs (1969). A total of 954 samples for 1976 and 637 samples for 1977 are represented, with the average number of samples per sampling date as follows: leaves, 11, grass-broadleaves, 14; litter-moss, 14; and soil, 4. Each bar is divided into two parts. The mean is above the line and its corresponding standard error below the line. Time is represented by the Julian date with upward directed arrows indicating spray application dates. Downward directed arrows above the bars indicate dates and amounts of rainfall in millimeters. (These data are also given in Tables I-1 and I-2.) The concentration scale is designed so that the highest bar for a given layer, over both canopy and alley regions, is nearly full scale.

The concentration of dislodgeable pesticide residue found in a given layer at any point in time throughout the season is a function of two processes: movement and attenuation. Attenuation is thought to include all degradative processes (chemical, photochemical, and microbial), airborne loss, penetration into plant subsurfaces, and irreversible soil binding (Ebling, 1963; Hull, 1970; Katan et al., 1976). Movement mainly redistributes the pesticide within the orchard. This redistribution, primarily by rainfall, is confounded with the attenuation processes, making determination of attenuation rates in the field difficult. A treatment of this problem using mathematical modeling techniques is described in Chapter II. An "eyeball" examination of these data indicates contrasting rates of both movement and attenuation among the various vertical strata and horizontal regions of the orchard. Comparison of leaf pesticide residues for the first spray period in 1976 (Figure I-3a) with leaf pesticide residues for the first spray period in 1977 (Figure I-4a) shows that the residues remaining after eleven days in 1977 are roughly two thirds the value of those pesticide residues remaining after 12 days in 1976. This difference is possibly due to the 20 mm and 25 mm rainfall events occurring in the interval between pesticide application and the sampling eleven days later in 1977, while no rain fell during the first spray period of the 1976 season. That rainfall is responsible for the reduction of foliar residue deposits has been suggested by a number of researchers, many of the earlier studies are summarized by Ebling (1963). In more recent studies, McMechan et al. (1972) reported that azinphosmethyl applied as a wettable powder formulation to apples was lost at a much more rapid rate from foliage during wet weather as opposed to dry. Similar results were reported by Williams (1961) for azinphosmethyl and carbaryl applied to apples, and by Thompson and Brooks (1976) for dislodgeable residues of azinphosmethyl and four other organophosphate insecticides applied as emulsifiable concentrates to oranges in Florida. Gunther et al. (1977) also noted the influence of rainfall on the decline of parathion dislodgeable residues applied as a wettable powder formulation to oranges in California. Nigg et al. (1977) used multiple linear regression to examine the relationship between residue decline of ethion dislodgeable residues (applied as E.C.) and the variables: degree-days, cumulative leaf wetness, and ordinary time. They found, for the experiment where rainfall occurred, that residue decay was most highly correlated with cumulative rainfall ($r^2 = .963$). In the present study, the leaf residue data also show that rainfall had a significant effect on pesticide residues in the tree. This is indicated by the results of a 23 mm rain occurring six days after the second spray application, which reduced the residue levels to less than half their former value. Similar results were reported by McMechan et al. (1972) for rainfall events occurring much closer to application. In their study, a 17.5 mm rainfall (1.8 mm/hr) that started six hours after a 50% WP azinphosmethyl application (.23 Kg a.i./Ha) to semi-dwarf apple trees, removed 41% of the initial deposit. A much lighter rainfall of 3.0 mm (0.9 mm/hr) that started five hours after a similar application, removed 12% of the initial deposit. Van Dyk (1976) examined the effect of artificial rainfall on parathion residues applied as both wettable powder and emulsifiable concentrate to orange, lemon, and grapefruit leaves and fruit. Rainfall was applied at 33 mm/hr. Factorial analysis of variance showed significant interaction ($P<0.01$) between parathion residues and the simulated rainfall. The type of formulation was not significant. This is not surprising considering the high rate of rainfall applied. By contrast, a 28 mm rain occurring 17 days following the third spray of the 1976 season (present study) had little effect on the apparent residue decline, suggesting that rainfall events occurring soon after application have a greater influence on leaf pesticide dislodgeable residue levels. This phenomenon has also been suggested by Ebling (1963), McMechan et al. (1972) for azinphosmethyl applied to apple foliage, and by Steffens and Weineke (1975) for ^{14}C azinphosmethyl applied to bean foliage. One theory that might explain this occurrence was first proposed by Gunther and Blinn (1955), also by Ebling (1963), and most recently by Elliott et al. (1977). These researchers suggest that pesticide deposits on foliar surfaces are lost at different rates due to the degree at which they adhere or penetrate the leaf surface. Initial rapid loss is a result of erosion of loosely bound deposits, possibly adsorbed to the formulations or dust on the plant. More tightly bound residues are lost primarily through volatilization, decomposition, and penetration into subsurface tissues. According to this theory, the percentage of the deposit that is loosely bound decreases rapidly following application. It is this fraction of the deposit that is most susceptible to erosion processes, including rainfall. As the loosely bound residues are lost, those more tightly bound residues that remain are less susceptible to loss with rainfall.

Comparison of 1976 canopy leaf residue data (Figure I-3a) with canopy grass-broadleaves residue data (Figure I-3b) shows little difference in residue decline, under the no-rainfall conditions of the first spray period. The effect of the 23 mm rain in the second spray period of the 1976 season on residue decline in the grass-broadleaves was much less than was seen in the canopy leaves (Figure I-3a). This might indicate that in addition to pesticide moving downward out of the grass-broadleaves with rainfall, pesticide is moving in from the tree above. Comparison of canopy litter-moss pesticide residues during the first spray period of 1976 (Figure I-3c) with those residues found in the grass-broadleaves (Figure I-3b) shows a marked difference in residue decline, as pesticide levels remain at a rather constant level throughout the spray period. This would suggest that under no-rainfall conditions, pesticide is moving into this layer at the same rate that pesticide is moving out and/or being attenuated. An alternative hypothesis would be no movement and no or very slow attenuation, which seems highly unlikely. Residue levels in the canopy litter-moss layer increased following the 23 mm rainfall event occurring during the second spray period of the 1976 season, again suggesting movement of pesticide into the litter-moss from layers above, in amounts greater than movement out and/or attenuation losses. In

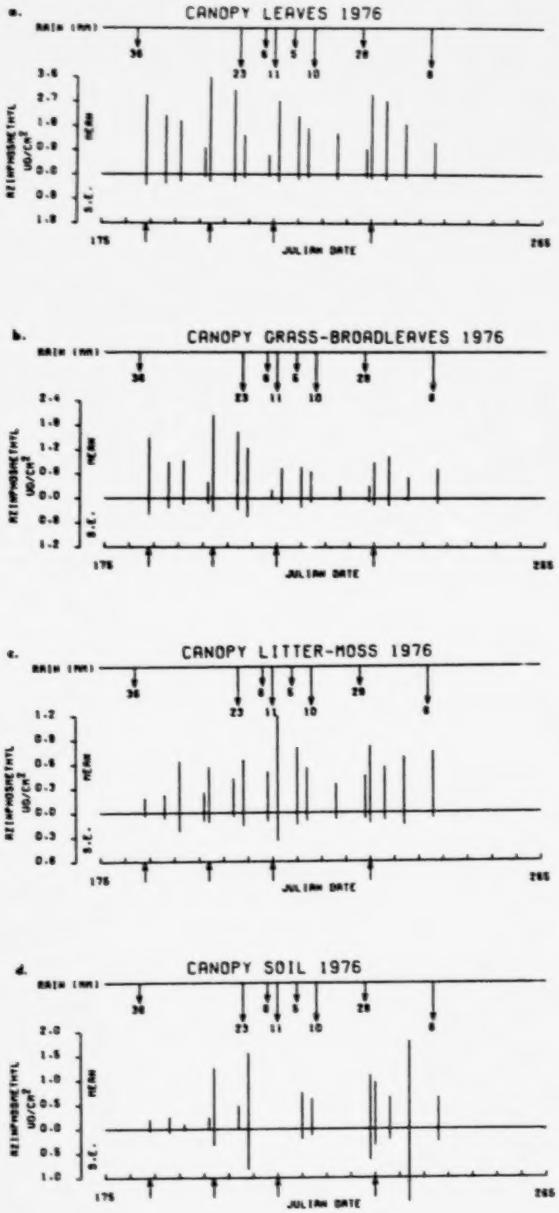


Figure I-3(a-d). Azinphosmethyl Dislodgeable and Soil Resiues for the Canopy Region, 1976 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (μg/cm^2) is above the line and its corresponding standard error (S.E.) below the line.

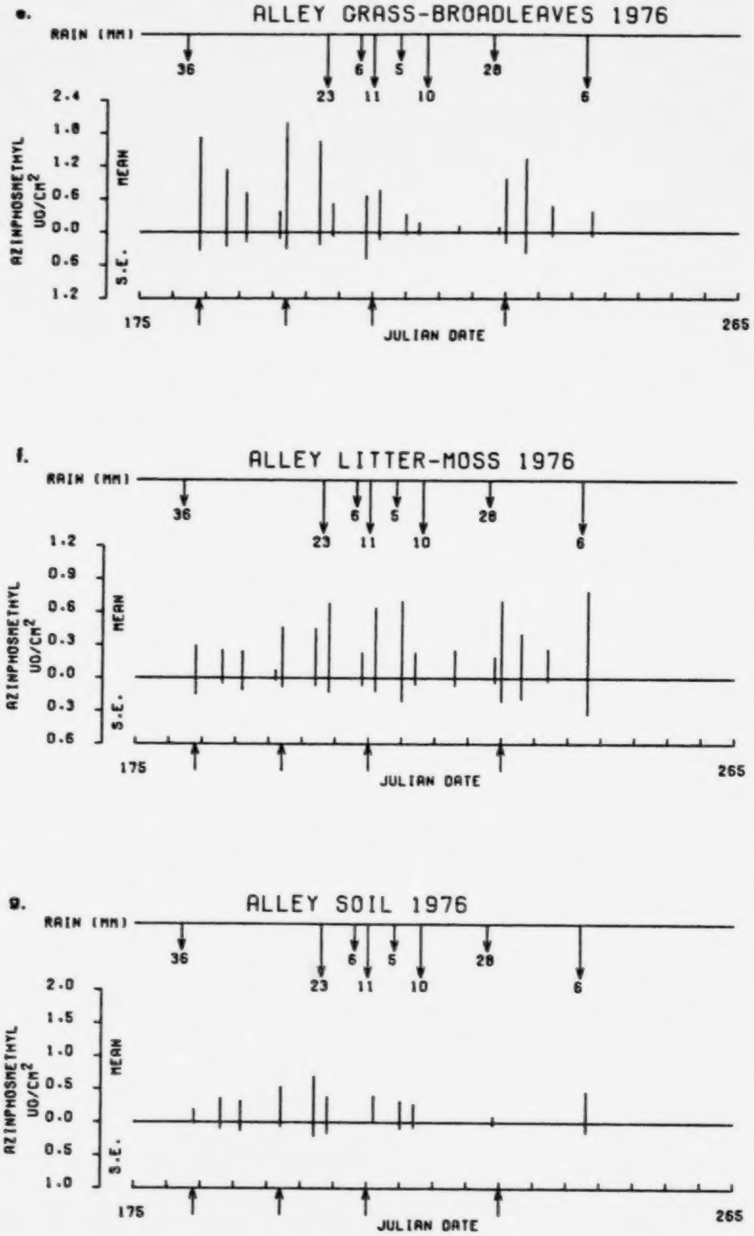


Figure I-3(e-g). Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1976 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.

general, canopy litter-moss residue values remained fairly constant throughout both the 1976 and 1977 seasons. Under no-rainfall conditions (first spray period, 1976 season, Figure I-3d), canopy soil residues did not increase with time following application as did the litter-moss residues. As azinphosmethyl has been shown to degrade faster in non-sterile soils as compared to sterile soils (Yaron et al., 1974), microbial degradation may play an important role in losses from this layer. In addition, root uptake and translocation (Al-Adil et al., 1973) may have been partially responsible for the observed soil residue pattern. Pesticide movement into the canopy soil with rainfall is again pronounced, as indicated by the 23 mm rainfall event during the second spray period of the 1976 season (Figure I-3d). The first spray period of the 1977 season shows canopy soil residue levels increasing with each rainfall event (Figure I-4d).

Alley grass-broadleaves pesticide residues show a systematic decline over the first spray period of the 1976 season (Figure I-3e). The decline is slightly steeper than the decline shown for canopy grass residues during the same no-rainfall period (Figure I-3b). This difference is probably due to less pesticide movement from the trees into the alley grass-broadleaves. Increased attenuation losses in the alley regions due in part to greater exposure to wind and solar radiation must also be considered. Taylor et al. (1977) in discussing factors influencing dieldrin volatilization from orchard grass, cited solar radiation as the most significant. Associated surface temperatures may also influence rates of chemical and microbial degradation and foliar uptake (Ebling, 1963; Hull, 1970). Azinphosmethyl applied to plant surfaces has been shown in one study (Liang and Lichtenstein, 1976) to be susceptible to photodegradation by sunlight. This degradative pathway is directly related to solar radiation. Rainfall effects are clearly shown when comparing alley grass residue to decline for the first spray period in 1976 (Figure I-3a) with the first spray period of the 1977 season (Figure I-4e). The difference in rainfall effects between canopy grass-broadleaves and alley grass-broadleaves is shown in the second spray period of the 1976 season (Figures I-3b and I-3e) which indicates that the pesticide movement, following the 23 mm rainfall event, out of the alley grass-broadleaves is probably greater due to direct exposure to rainfall, and also that there is little or no pesticide movement in from the trees. Again, differential attenuation due to shading cannot be disregarded. Alley litter-moss pesticide residues show a definite decline during the first and last spray periods of the 1977 season (Figure I-4c), the alley litter-moss residue values show a decline, indicating that residue movement out and/or attenuation is greater than residue movement into this alley layer. Alley soil residues for the first spray period of the 1976 season (Figure I-3g) are similar to canopy soil residues for the same period (Figure I-3d, note the difference in scaling). There appears to be a decrease in alley soil residue levels following the 23 mm rain during the second spray period of the 1976 season (Figure I-3c) whereas the canopy soil residues (Figure I-3d) increase following this rainfall event. The high variability of these data discourages speculation as to the processes taking place. The general pattern of these residue levels over the season, characterized by a buildup of residues toward mid-season, is surprisingly similar to the azinphosmethyl orchard soil residue pattern reported by Kuhr et al. (1974). A general observation of the data presented in Figure I-3 indicates that, as the season progressed, the interrelationship between pesticide movement and attenuation became more difficult to follow. This complexity is possibly a function of changes in weather patterns in addition to rainfall (temperature, humidity and wind). Gunther et al. (1977) attempted to relate temperature data to the decline of azinphosmethyl residues applied to citrus in southern California. They found it difficult to make any meaningful interpretation of the data, but stated that azinphosmethyl dissipation was slightly more rapid during warmer weather. No correlations between residue data and temperature or humidity were attempted in the present study, but weather data were provided for possible future use (Figures I-4 and I-5). Changes in plant physiology and soil microbial activity or a buildup of tightly bound or penetrated residues, may also have an effect on pesticide residue dynamics throughout the season.

However, from the limited analysis of the data, there is some indication that azinphosmethyl is redistributed throughout the orchard with time following application. Redistribution is indicated during periods without rainfall, but is more pronounced following rainfall events. Little more information can be gained without the aid of a more sophisticated technique of analysis. Such an analysis of the data is presented in Chapter II. Using mathematical modeling techniques, the change in observed residue levels in each layer and region is estimated as a function of both movement and attenuation.

Information on pesticide concentrations as a function of movement and attenuation is essential to the estimation of possible exposure to the biota of this agroecosystem. If pesticides are to be used in an effective manner in conjunction with biological control techniques, possible exposure to beneficial populations, as well as the target species, must be better understood under a variety of climatic conditions.

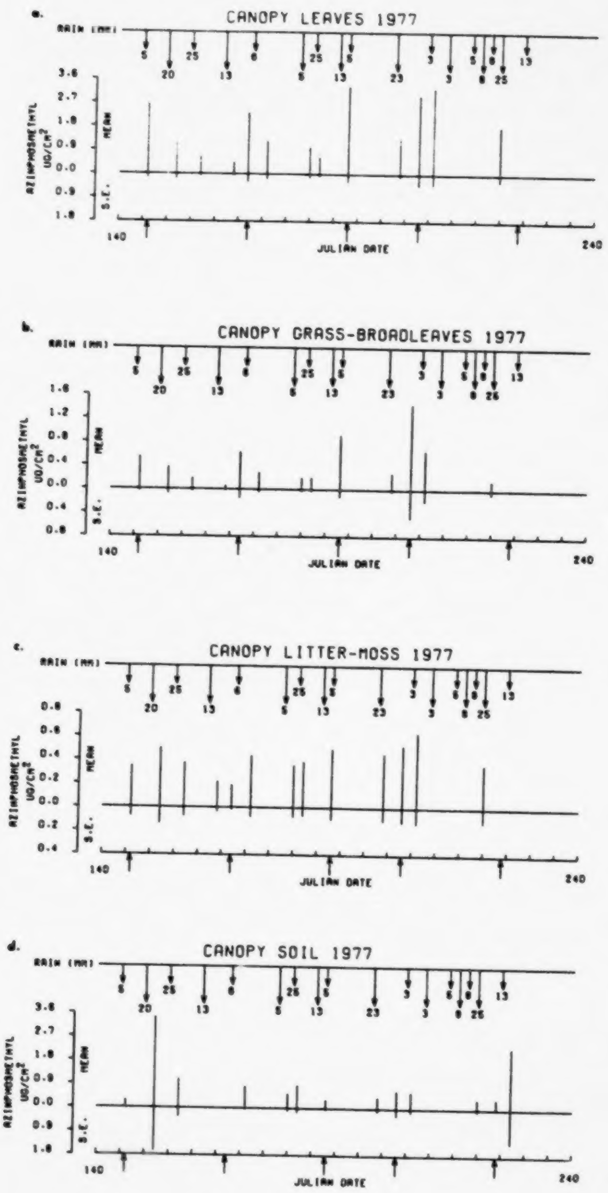


Figure I-4(a-d). Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1977 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (μg/cm^2) is above the line and its corresponding standard error (S.E.) below the line.

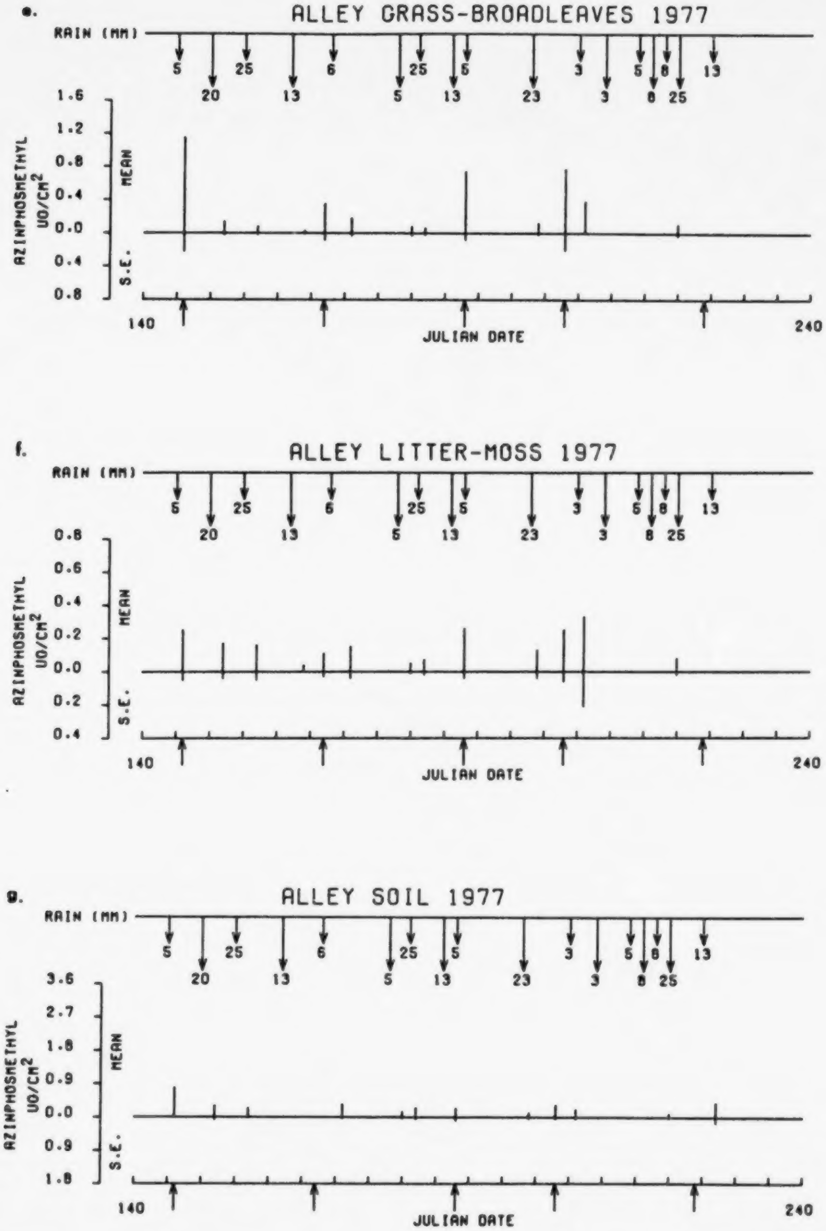


Figure I-4(e-g). Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1977 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (μg/cm^2) is above the line and its corresponding standard error (S.E.) below the line.

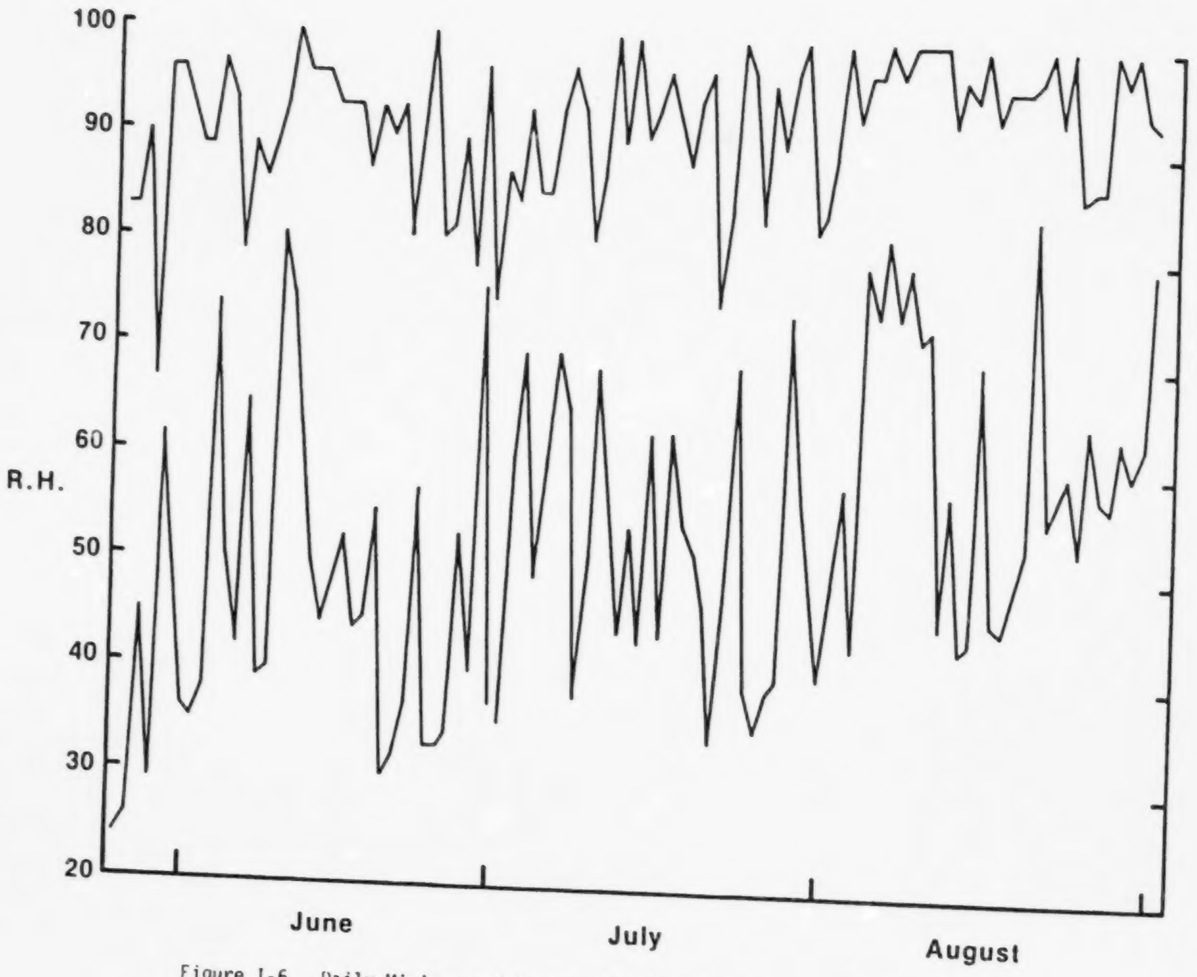


Figure I-6. Daily Minimum and Maximum Relative Humidity, 1976 Season

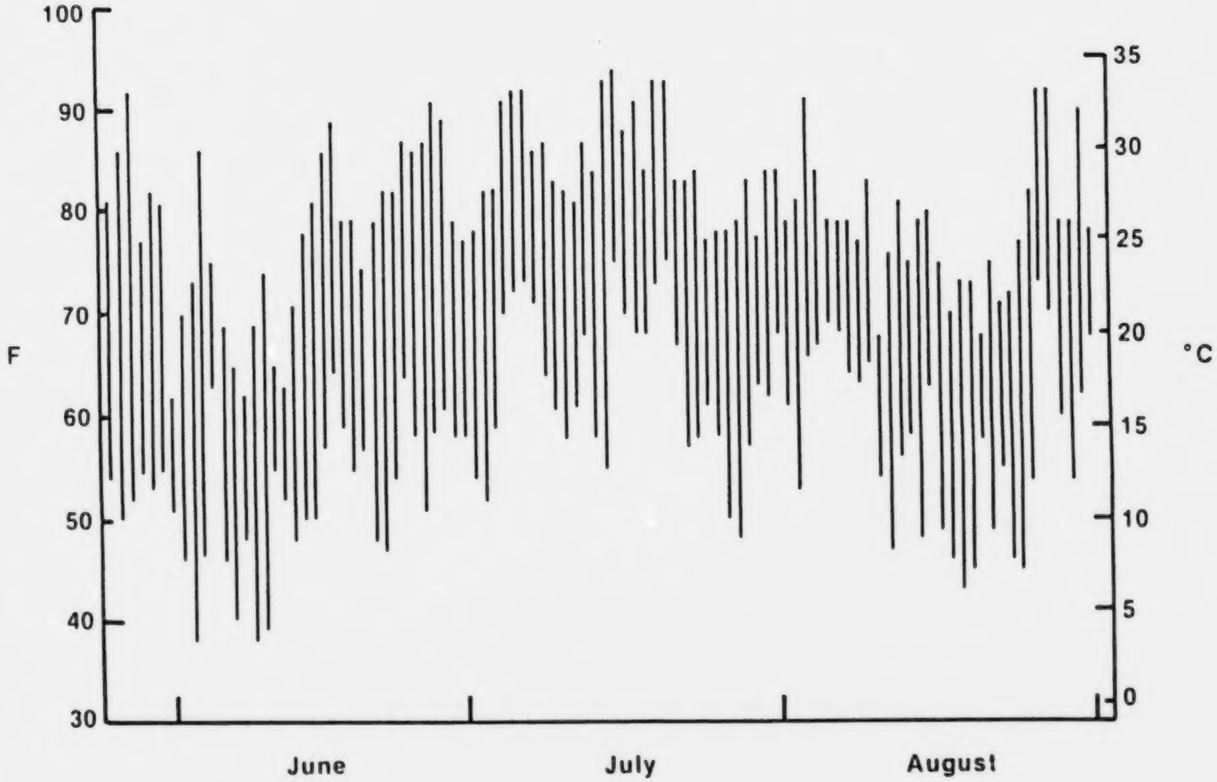


Figure 1-7. Daily Temperature Range, 1977 Season

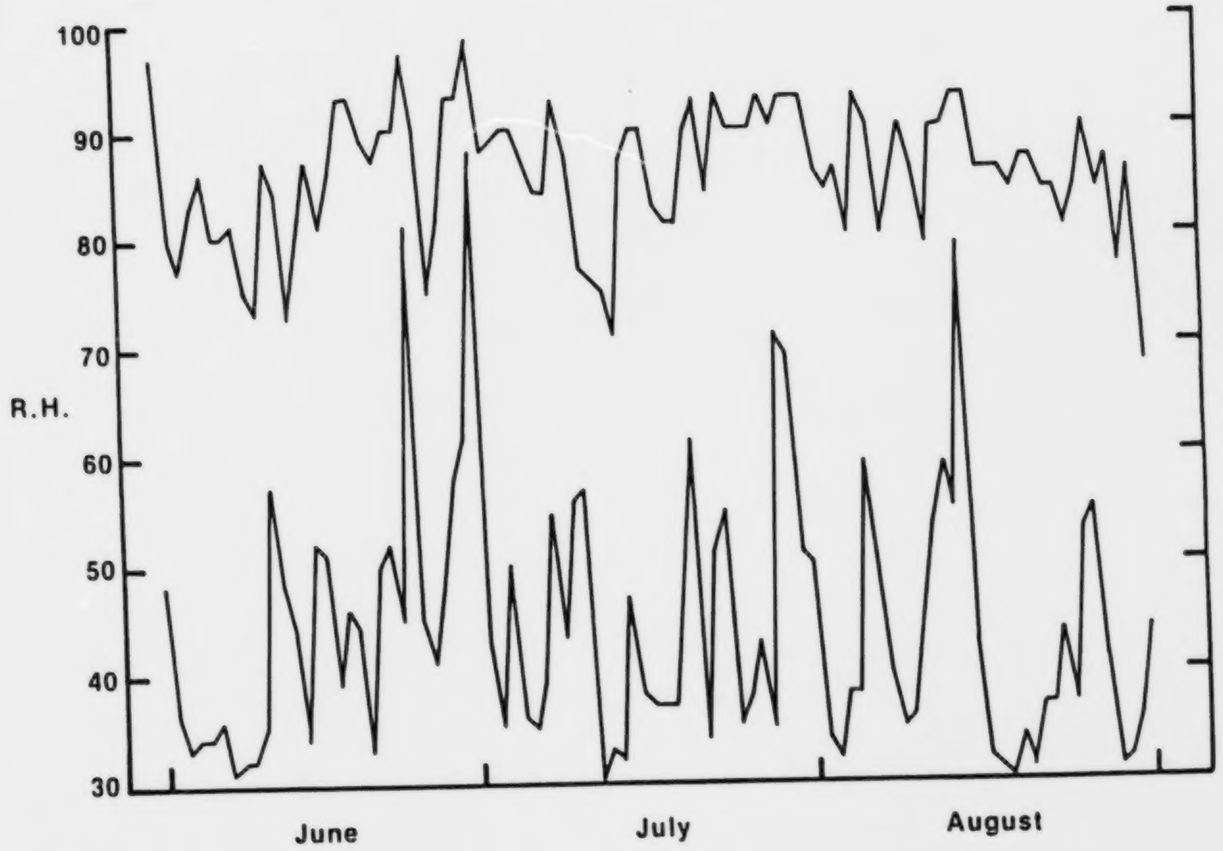


Figure I-8. Daily Minimum and Maximum Relative Humidity, 1977 Season

CHAPTER II

PARAMETERIZATION OF THE AZINPHOSMETHYL FATE MODEL

INTRODUCTION

In Chapter I a description of the field data collected on the distribution, movement, and attenuation of azinphosmethyl in an experimental apple orchard was given. These data were gathered specifically in order to allow development, refinement, and parameterization of a model describing the spatial and temporal distribution of azinphosmethyl in the orchard in response to rainfall. While the time series of concentrations observed were reported in the earlier part, the model and the parameterization process, together with the parameter values generated, are described in this part. Validation of this model using a third season's data is presented.

The form of this model was chosen to allow: (1) use of model output to provide pesticide exposures for models of organisms dwelling in the orchard floor (Goodman, 1982) and (2) future development to represent the dynamics of other pesticides and the effects of additional environmental factors.

THE MODEL

In order to structure the experimental program and the data analysis, a conceptual model for the distribution, movement, and fate of the pesticide in the orchard was formulated. Information gathered has resulted in continual refinements of the model structure. The conceptual model utilizes a spatial subdivision of the orchard into a canopy region and three alley regions (Figure 2 of Chapter I).

Vertically, four strata (not necessarily all present at a given sampling location) are identified. These are called tree, grass-broadleaves, litter-moss, and soil.

The conceptual model (see Figure II-1) describes the dynamics of the pesticide from its spray application to its ultimate disappearance from the orchard via drift, attenuation (including airborne loss, photolysis, chemical degradation, microbial degradation, and penetration of surface residues) and runoff. Each day, a vector C of concentrations of pesticide in each of seven regions (two horizontal by four vertical, minus one for non-existent alley trees) is calculated, based on management actions (spraying, mowing) and rainfall. Figure II-1 describes the processes affecting the pesticide concentration in only one of the seven regions.

For analysis of the field data, the processes in Figure II-1 are lumped into three categories: inital distribution, movement, and attenuation. Movement is further subdivided according to rainfall intensity (none, light, and heavy). The mathematical forms of the various components of this model are described below:

(1) Initial Distribution

The spray rate (in Kg/ha) is supplied as an input. Drift, including losses from the orchard during spraying and up to the time of

Preceding page blank

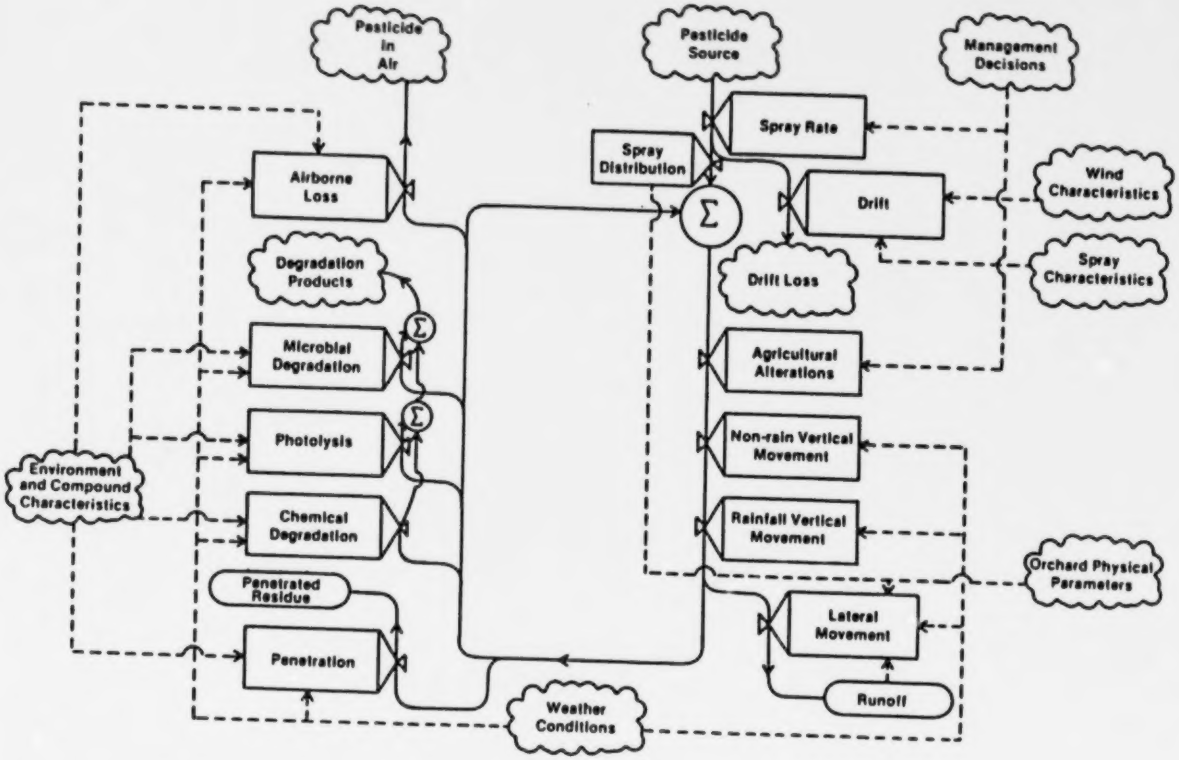

Pesticide in Air
Pesticide Source
Management Decisions
Spray Rate
Spray Distribution
Airborne Loss
Wind Characteristics
Drift
Σ
Degradation Products
Drift Loss
Spray Characteristics
Σ
Microbial Degradation
Agricultural Alterations
Σ
Photolysis
Non-rain Vertical Movement
Environment and Compound Characteristics
Chemical Degradation
Rainfall Vertical Movement
Penetrated Residue
Orchard Physical Parameters
Lateral Movement
Penetration
Runoff
Weather Conditions

Figure II-1. Conceptual Model for the Distribution, Movement, and Attenuation of Azinphosmethyl in an Apple Orchard

post-spray sampling, was estimated using mass conservation, based upon the known application rate, estimated pre-spray residue levels, and measured residues following application (see Chapter I). The proportion drift averaged .376 ± .149 over the three seasons. Because the standard deviation observed among the data was higher than anticipated, an attempt was made to relate the drift loss to wind speed at the time of application from the available data. Mean wind speeds during application were estimated from data of the Michigan Weather Service, Grand Rapids, Michigan. The following relationship was determined:

$$D = .021\ WS + .091 \quad (r^2 = .475)$$

where D is proportion drift and WS is wind speed in km/hr.

The residue deposited in the orchard is apportioned into the seven regions according to a spray distribution vector, in which each entry specifies the proportion of the spray that is captured by the corresponding region, and added to any remaining residue from earlier sprays in the pesticide concentration vector C. All units are expressed as μg pesticide/cm^2 ground area.

(2) Attenuation

Attenuation is treated in the model as a set of daily proportion losses--a single proportion for each layer. Thus it is conveniently representable as a diagonal matrix A which pre-multiplies the pesticide distribution vector C, a seven-element column vector containing the concentration of pesticde (μg/cm^2) in each region at a particular time. Each day, attenuation is extracted via equation (1):

$$C(after) = (I-A)C(before) \tag{1}$$

where I is the 7 x 7 identity matrix.

C_4 and C_7, the pesticide concentrations in canopy and alley soils, respectively, represent total soil residues, while C_1,C_2, C_3, C_5, and C_6 represent only dislodgeable residues. Thus the attenuation for non-soil layers includes surface penetration of residues.

(3) Movement

Daily redistribution of the pesticide within the orchard is modeled using three matrices to pre-multiply the pesticide distribution column vector C. Daily movement not attributed to rainfall is modeled by equation (2):

$$C(after) = PC(before) \tag{2}$$

where P is a 7 x 7 column-stochastic lower triangular matrix known as the non-rainfall pure movement matrix. The matrix P is restricted to containing at most 19 non-zero entries, as the tree layer is the only canopy layer from which movement to alley layers is modeled, so $P_{ij} = 0$, for i = 5,6,7 and j = 2,3,4.

Several parameters are necessary to adequately describe a rainfall event; for example, duration, average intensity, peak intensity, etc. Unfortunately the small number of rainfall events during a spray season precluded using so fine a description. Rainfall events were classified on a daily basis into only two categories (heavy and light) in order to obtain enough instances of each category to parameterize the model. Heavy rain was defined as any event of more than 10 mm rainfall or more than 5 mm/hour in a day, with other measurable rain classified as light. Equations (3) and (4) show the pesticide redistributions caused by heavy and light rainfall, respectively:

$$C(\text{after}) = HC(\text{before}) \tag{3}$$

$$C(\text{after}) = LC(\text{before}) \tag{4}$$

where H and L are 7x7 column-stochastic lower triangular matrices.

As in equation (1), H and L do not model movement between alley and canopy ground layers; thus pesticide movement with overland runoff is not included in these equations.

Attenuation and non-rainfall movement were modeled (and parameterized) as daily phenomena. Thus, to represent the natural changes in pesticide distribution from one day to the next, (C(k) to C(K+1)), exactly one of the following relationships is used:

$$C(k+1) = P(I-A)C(k) \quad \text{(no rain)} \tag{5}$$

$$C(k+1) = L\,P(I-A)C(k) \quad \text{(light rain)} \tag{6}$$

$$C(k+1) = H\,P(I-A)C(k) \quad \text{(heavy rain)} \tag{7}$$

METHODS FOR PARAMETER ESTIMATION

This section describes the techniques used to estimate the model parameters from the data base of field determinations. The routines described are designed to be used repeatedly, i.e., as entries are added to the data base, new parameters including their effects can be quickly generated. This capability for dynamic reparameterization of the model gives it the flexibility to begin with relatively few crude data, producing preliminary outputs, and to produce more accurate results as the data base grows.

Data Base

The data base consists of a large number of sequential disk files, which are updated and utilized by various programs. Rainfall data, orchard plot physical characteristics, and records of samples analyzed for pesticide are stored in these files. Figure II-2 shows how sample and target data, entered as "raw" outputs from gas chromatograph measurements, are transformed into new files of "processed" sample and target data. In this stage, appropriate corrections for analytical technique, sample weight, averages across samples, etc. are made, yielding files suitable for use in calculating the model parameters. Figure II-3 is a flowchart of the process of calculating the parameters using the "processed" files. Files used by a given routine are shown with a dashed arrow into the routine, and files produced are shown with a dashed arrow to the files. Flow of the program is via the solid arrows.

Subroutines LEAF and AREA perform needed conversions of some residue measurements (for example, from μg pesticide/cm^2 leaf area to μg pesticide/cm^2 ground area). TARGETS uses "processed" target values to determine a proportion of pesticide reaching each plot and region.

The process of parameterizing this model continues with FINDEV, a subroutine which searches the data files for sets of samples useful for calculating redistribution and losses of the pesticide. For estimating loss and movement in the absence of rain, it prepares a file of sample sets each of which consists of a vector of concentrations (in each region and layer) at the beginning of a non-rainfall interval and a similar vector at the end of the interval. Of course, either rain or a spray intervening will exclude a

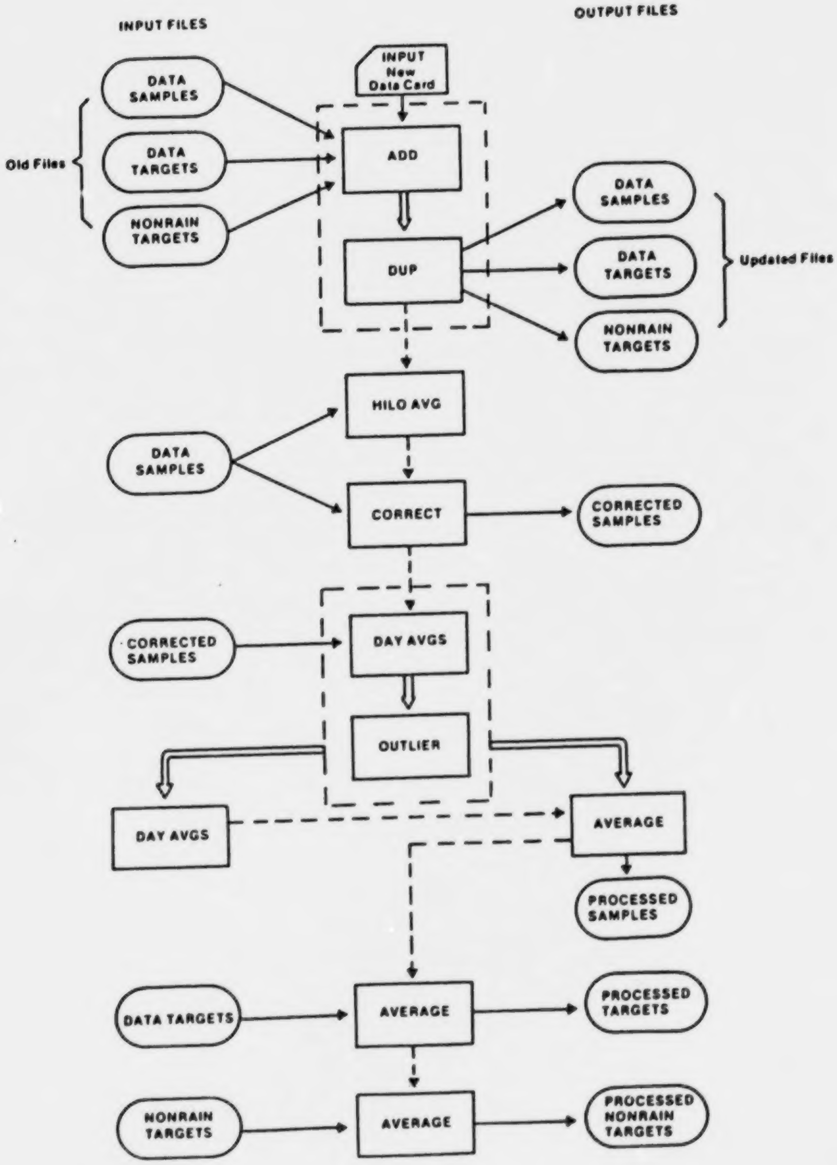

INPUT FILES
OUTPUT FILES
INPUT New Data Card
DATA SAMPLES
Old Files
DATA TARGETS
NONRAIN TARGETS
ADD
DUP
DATA SAMPLES
DATA TARGETS
NONRAIN TARGETS
Updated Files
HILO AVG
DATA SAMPLES
CORRECT
CORRECTED SAMPLES
CORRECTED SAMPLES
DAY AVGS
OUTLIER
DAY AVGS
AVERAGE
PROCESSED SAMPLES
DATA TARGETS
AVERAGE
PROCESSED TARGETS
NONRAIN TARGETS
AVERAGE
PROCESSED NONRAIN TARGETS

Figure II-2. Flow Chart Showing Data Processing to Yield Files Suitable for Use in Model Parameterization

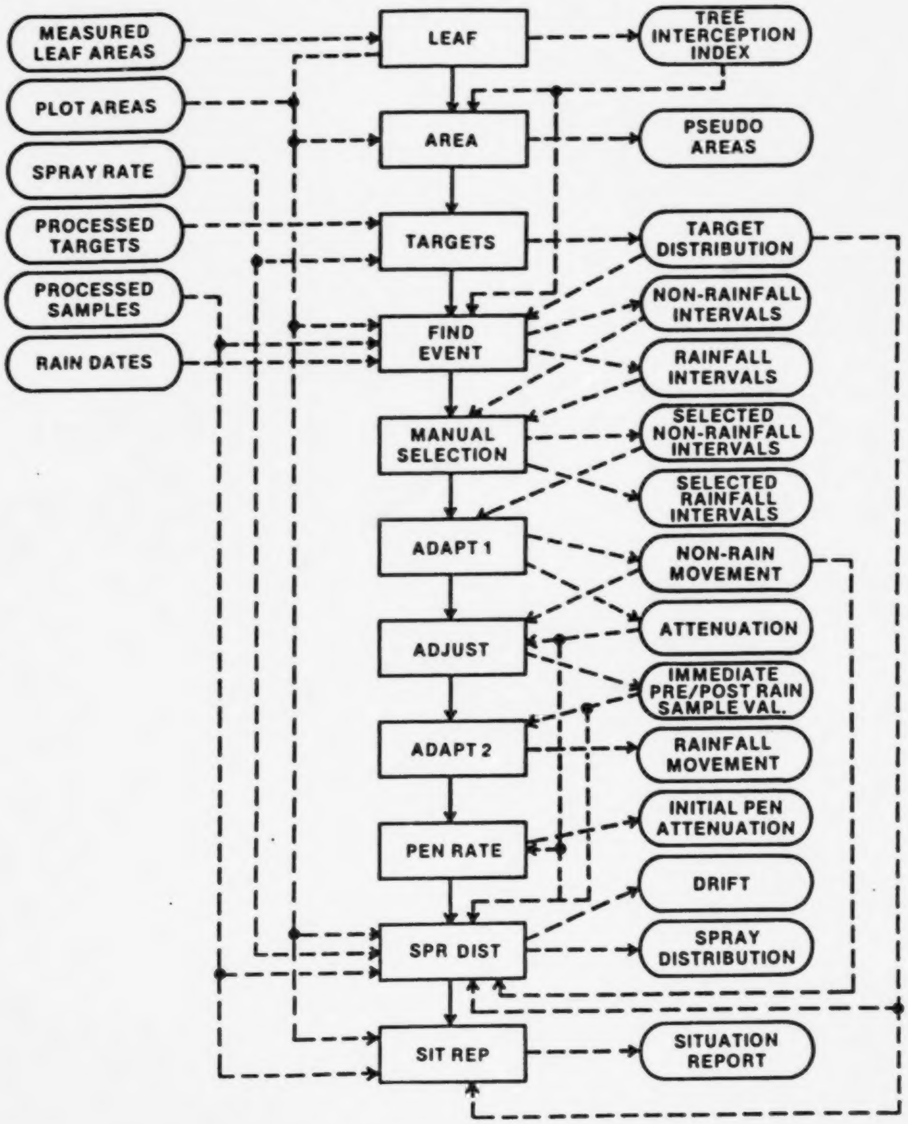

MEASURED LEAF AREAS
PLOT AREAS
SPRAY RATE
PROCESSED TARGETS
PROCESSED SAMPLES
RAIN DATES
LEAF
AREA
TARGETS
FIND EVENT
MANUAL SELECTION
ADAPT 1
ADJUST
ADAPT 2
PEN RATE
SPR DIST
SIT REP
TREE INTERCEPTION INDEX
PSEUDO AREAS
TARGET DISTRIBUTION
NON-RAINFALL INTERVALS
RAINFALL INTERVALS
SELECTED NON-RAINFALL INTERVALS
SELECTED RAINFALL INTERVALS
NON-RAIN MOVEMENT
ATTENUATION
IMMEDIATE PRE/POST RAIN SAMPLE VAL.
RAINFALL MOVEMENT
INITIAL PEN ATTENUATION
DRIFT
SPRAY DISTRIBUTION
SITUATION REPORT

Figure II-3. Flow Chart of the Process of Calculating the Parameters Using the "Processed Files"

pair of sequential sample vectors from being used for this purpose. FINDEV also prepares similar files of vectors representing samples before and after rainfall events of various intensities to allow estimation of the effects of these rains on the pesticide distribution. As shown in the diagram, manual selection is utilized to determine rain events to be classified as similar, and to exclude sample dates which are unacceptable for the task to be performed (when numerous data are missing for a given sample date). The matrices A and P (equations (5), (6) and (7)) are determined from a matrix Q = P(I-A). After Q is found (see equation (9) below), the entries A_{ij} are calculated as:

$$A_{ij} = \sum_{k=1}^{7} Q_{ik},\ i=j;\ A_{ij} = 0, i \neq j,\ i = 1,\ldots,7;\ j = 1,\ldots,7$$

$$\text{Then } P = Q(I-A)^{-1} \qquad (8)$$

From equation (8), Q should relate the pesticide vector C(k) to C(k+1) for each day k_i on which no rainfall occurred. Thus, given matrices B = $[C(k_1)\ C(k_2)\ldots C(k_n)]$ and A = $[C(k_1 + 1)\ C(k_2 + 1)\ldots C(k_n + 1)]$, $k_i \in$ days without rainfall, the following relationship should hold:

$$A = QB. \qquad (9)$$

So long as at least seven sets of before/after concentrations are available, Q should be uniquely determinable using Gaussian elimination. However, owing to both random and systematic variations in the data sets, such a procedure did not produce a feasible solution. It is necessary to introduce additional constraints that a "best fit" must satisfy. Entries in Q must be restricted to the range [0,1], so that pesticide removed from a region is limited to what is available for movement. Also, because too few soil samples were analyzed to allow for a reliable solution for the pesticide attenuation rate in soils, a rate determined from the incubation of the orchard soil in the lab was introduced into the solution matrix before the remainder of the 19 were determined. Solution for the entries in Q to optimize the fit to all available data for non-rainfall intervals was carried out in program ADAPT1, using the adaptive optimization technique of Holland (1975), also described in DeJong (1980).

The optimization was done on a broadened version of equation (9) allowing varying intervals between sampling days, since:

$$C(k_i + m) = Q^m C(k_i),\ m \geq 1, \text{ so long as no rain falls on days } K_i,\ldots,K_{m-1}.$$

Once Q was determined, it was used, together with Equation (6) and data surrounding light rainfall events, to calculate L, the light rain movement matrix. Because samples were typically collected at intervals of three to five days, the effects of degradation and non-rainfall movement were removed from the data surrounding each rainfall before the rain effect could be determined. Using equations (5) and (6), we obtained:

$C(k_i + p + q) = Q^q\ L\ Q^p\ C(k_i)$, where C was known at days K_i and k_{i+p+q} and light rain occurred on day k_i+p. Thus $(Q^{-1})^q C(k_i+p+q) = L\ Q^p\ C(k_i)$, and matrices of before-and after-rainfall estimated concentration vectors were assembled as

$$A_L = [(Q^{-1})^{q_1} C(k_1 + p_1 + q_1)\ldots(Q^{-1})^{q_n} C(k_n + P_n + q_n)]$$

$$B_L = [(Q^{p_1} C(k_1)\ \ldots\ (Q^{p_n} C(k_n)]$$

and the matrix L in $A_L = L B_L$ was optimized by ADAPT2, a program similar to ADAPT1. It also solves, in an analogous fashion, for the heavy rainfall movement matrix H of equation (8).

Once the movement matrices are parameterized by the adaptive routines, the initial pesticide distribution for spray applications subsequent to the first application of the season are estimated. The attenuation and movement matrices are used, along with the residue distribution of the last sampling day of the preceding spray period, to estimate the dislodgeable residues present just prior to application. PENRATE (Figure II-3) calculates the estimate of the amount of surface-penetrated residues present at the time of application based upon its estimate of the dislodgeable residue and a ratio of surface-pentrated to dislodgeable residues. This ratio was determined from matched samples taken the last sampling day for selected spray periods over the 1976, 1977 and 1978 seasons. The surface-penetrated to dislodgeable residues and standard errors were as follows: leaves, 0.110 ± .003; grass, 1.075 ± .195; litter, 2.367 ± .263; moss, 1.701 ± .184. These ratios were multiplied by the appropriate dislodgeable residues to estimate the surface penetrated residues present just prior to application. To estimate the initial pesticide distribution, the estimates of dislodgeable and surface-penetrated residues present at the time of application were subtracted from the total residues measured the afternoon following application. Assuming these estimates are conservative (see Chapter I), drift is determined as the difference between the estimate of the amount deposited in the orchard at application and the amount applied. Using the method described above, the average proportion and standard deviation of the dose initially distributed to the orchard, for all spray applications over the three seasons (except two applications for which there was rainfall following the last sampling day of the preceding spray period) was .624 ± .149, giving an average drift estimate as reported earlier.

The final routine, situation report, produces a daily record of both measured and predicted residue values. The data are provided both tabular and graphical form, as shown in Figures II-8a-g.

RESULTS AND DISCUSSION

Parameterization of the Attenuation and Movement Matrices

The model was parameterized with azinphosmethyl residue data, collected over two seasons (1976, 1977) as previously described in Chapter I, plus a third season (1978). The matrices generated (for equations (1) to (4)) are shown in Figures II-4, II-5, II-6, and II-7. The matrices describe the daily attenuation and movement of pesticide under three specified rainfall conditions; none, light, and heavy. The no-rainfall movement matrix (P) shows some pesticide movement from the tree, possibly due to wind erosion, dew or guttation, with the majority of the residue being trapped in the litter-moss layer. Also of interest is the fact that the model estimates that equal amounts of residues (approximately 0.9%) move from the tree to the canopy litter-moss and alley litter-moss layers. Gunther et al. (1977) estimated the movement of parathion from orange trees to the ground over a five-day period to the less than 1% of the applied dose. In order to directly detect this movement in the orchard used in this study, filter paper targets were placed on the orchard floor (as described in Chapter I) for periods without rainfall of up to four days. Recovery of approximately 0.5% of initial tree residues confirmed the existence of some pesticide movement. The unkown rate of loss

ATTENUATION

CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
.049						
	.041					
		.167				
			.079			
				.067		
					.223	
						.079

Figure II-4. Azinphosmethyl Attenuation Matrix

		FROM						
NON-RAINFALL MOVEMENT MATRIX		CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
TO	CANOPY LEAVES	.983						
	CANOPY GRASS-BROADLEAVES	0.0	.935					
	CANOPY LITTER-MOSS	.008	.065	.907				
	CANOPY SOIL	0.0	0.0	.093	1.0			
	ALLEY GRASS-BROADLEAVES	0.0				.973		
	ALLEY LITTER-MOSS	.009				.027	.996	
	ALLEY SOIL	0.0				0.0	.004	1.0

Figure II-5. Azinphosmethyl Non-Rainfall Movement Matrix

FROM

	LIGHT RAINFALL	CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
	CANOPY LEAVES	.932						
	CANOPY GRASS-BROADLEAVES	.030	.747					
	CANOPY LITTER-MOSS	.002	.071	1.0				
TO	CANOPY SOIL	.036	.182	0.0	1.0			
	ALLEY GRASS-BROADLEAVES	0.0				.869		
	ALLEY LITTER-MOSS	0.0				0.0	1.0	
	ALLEY SOIL	0.0				.131	0.0	1.0

Figure II-6. Azinphosmethyl Light Rainfall Movement Matrix

	HEAVY RAINFALL	FROM						
		CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
TO	CANOPY LEAVES	.822						
	CANOPY GRASS-BROADLEAVES	.020	.613					
	CANOPY LITTER-MOSS	.096	0.0	1.0				
	CANOPY SOIL	.008	.387	0.0	1.0			
	ALLEY GRASS-BROADLEAVES	.027				.280		
	ALLEY LITTER-MOSS	0.0				.447	1.0	
	ALLEY SOIL	.027				.273	0.0	1.0

Figure II-7. Azinphosmethyl Heavy Rainfall Movement Matrix

from the targets precludes a direct assessment of the movement rate based only on these data.

Figure II-4 shows an attenuation rate for azinphosmethyl dislodgeable residues in the tree of 4.9% day^{-1}. Hall et al. (1975) examined the loss of azinphosmethyl dislodgeable residues applied to apples using two types of air blast sprayers. Trees were sprayed on one side only and each tree was divided into nine sites for sampling. The average residues remaining for sites one to five (which most closely correspond to the tree area sampled in the present study) over a 14-day period were used to determine the loss rate. Rates determined were 7.6% day^{-1} (r^2 = .914) for the high flow-rate application and 5.5% day^{-1} (r^2 = .887) for the low air flow-rate application. These loss rates are higher than the attenuation rate alone as determined in the present study, but are in excellent agreement with the overall loss rate of azinphosmethyl dislodgeable residues from the tree of 6.7% day^{-1} (obtained by summing attenuation and movement from the tree under dry conditions). These results suggest that approximately 25% of the daily loss of azinphosmethyl dislodgeable residues from the tree is redistributed within the orchard, under dry conditions.

Figure II-5 shows that less movement occurred from the grass-broadleaf to litter-moss layer in the alley region than in the canopy, suggesting that conditions under the tree canopy may be more favorable to movement, in the absence of rainfall. The attenuation rate for the canopy grass-broadleaves is similar to that observed in the tree. However the attenuation rate for the alley grass-broadleaf layer is considerably higher. Increased exposure to solar radiation resulting in higher surface temperatures, which in turn influence losses by volatilization, degradation, and plant uptake (Ebling, 1963; Hull, 1970; Bukovac, 1976) may be responsible for the observed difference. Movement out of the canopy litter-moss layer in the absence of rainfall was similar to that from the grass-broadleaves, with virtually no movement from the alley litter-moss. Attenuation rates observed in the litter-moss layer are higher than might be expected, but little is known about pesticide attenuation on these surfaces. Again the rate observed in the alley was greater than that in the canopy. The reason for this difference is thought to be the same as for the grass-broadleaf layer. The laboratory-determined rate for azinphosmethyl attenuation in soil (7.9% day^{-1}) is only an approximation of the field rate. However this rate is in rough agreement with the rate of 6.3% day^{-1} determined from the field data of Kuhr et al. (1974), in which samples were taken from beneath apple trees in an upstate New York orchard (ignoring any movement of azinphosmethyl into the soil). A loss rate of 5.8% day^{-1} was determined from the field data of Schulz et al. (1970), in which azinphosmethyl was applied as an emulsifiable concentrate to the soil surface. The experiment was run in the early spring in Wisconsin (soil temperature 5-15°C). Only a general comparison can be made with these field studies, as soil type, pH, available moisture, ground cover, and temperature, as well as amount and mode of application, may influence azinphosmethyl loss from soil (Hamaker, 1972;Schulz et al., 1970).

Rainfall-induced losses of azinphosmethyl and other deposit residues in orchards have been indicated by a number of researchers (McMechan et al., 1972; Williams, 1961; Thompson and Brooks, 1976; Gunther et al., 1977; Nigg et al., 1977). The influence of rainfall on the removal of azinphosmethyl from apple foliage is discussed in Chapter I. The present treatment of the data calculates azinphosmethyl loss as a function of heavy or light rainfall (as defined above). No attempt was made to relate susceptibility to rainfall removal with the age of the residue deposit. Figures II-6 and II-7 show that approximately 7% and 12% of the residues are moved out of the tree by light and heavy rainfall, respectively. The light rain moves all these residues into the canopy region, while the heavy rainfall moves two-thirds to the canopy and one-third to the alley region. Values for proportions moved to the individual layers are probably not as reliable, but generally light rain moves the residues to the canopy grass-broadleaf and soil layers while the heavy rain moves the largest proportion of the canopy litter-moss layer. Canopy and alley grass-broadleaves and alley soil receive lesser amounts. Eighteen and 38% of the residues deposited on the canopy grass-broadleaf layer are moved to the soil following light and heavy rainfalls, respectively. Thirteen percent is moved from the alley-grass-broadleaves to the soil as a result of light rainfall, whereas 27% is moved as a result of heavy rainfall. The largest proportion of alley grass-broadleaf residue (45%) is moved to the litter-moss following a heavy rainfall. No movement is indicated from the litter-moss layer as a result of either light or heavy rainfall.

Certain types of movement are difficult to distinguish based on the available data. For example, a large amount of movement from the canopy grass-broadleaves to the soil, accompanied by a similar amount of movement from the tree to the canopy grass-broadleaves, can produce the same result as a direct movement from the tree to the soil. Only a widely varying set of initial pesticide distributions would enable the parameterization routes to distinguish these two processes definitively. However, in the operation of the model, the net resulting distribution will be similar in either case, so long as the initial distribution is similar to the one used to parameterize the model. More credibility should be attached to the model-generated distributions than to the individual matrix entries.

Comparison of the Model Outputs with the Field Data

Figures II-8(a-g) show a test of the model's predictions as compared to the field data obtained during the 1978 season. The continuous lines (solid or dashed) represent the model's daily prediction of azinphosmethyl dislodgeable foliar and soil residues in each region for the 1978 season and are directly comparable with the vertical lines showing measured residue levels (and standard errors) in 1978. All residues are expressed as $\mu g/cm^2$ ground area, including the tree residues, to maintain a material balance in the transfer of pesticide between layers and regions of the orchard. The models were driven by 1978 rainfall data (shown as descending arrows in the figures) and the 1978 spray application rates (shown as ascending arrows). The matrices used to generate the solid line in Figure II-8a-g were calculated using 1976 and 1977 data only, while the dashed line was generated from the matrices (Figures II-4, II-5, II-6, and II-7) calculated using data from all three years. The 1978 sample data therefore represents an independent set of field data, collected from the same orchard plots, by which to judge the predictive capability of the model parameterized using data from the 1976 and 1977 seasons (continuous solid line).

In the tree leaves and grass-broadleaf layers, to which over 80% of the residues are initially deposited, the trends in the data are predicted quite well. Lower residue levels and the high variability in the amount and composition of the litter-moss layer are most likely responsible for the difficulty in predicting attenuation and movement in and out of this layer. In addition, the overall predictive capability of the model should improve with a better estimate of drift loss.

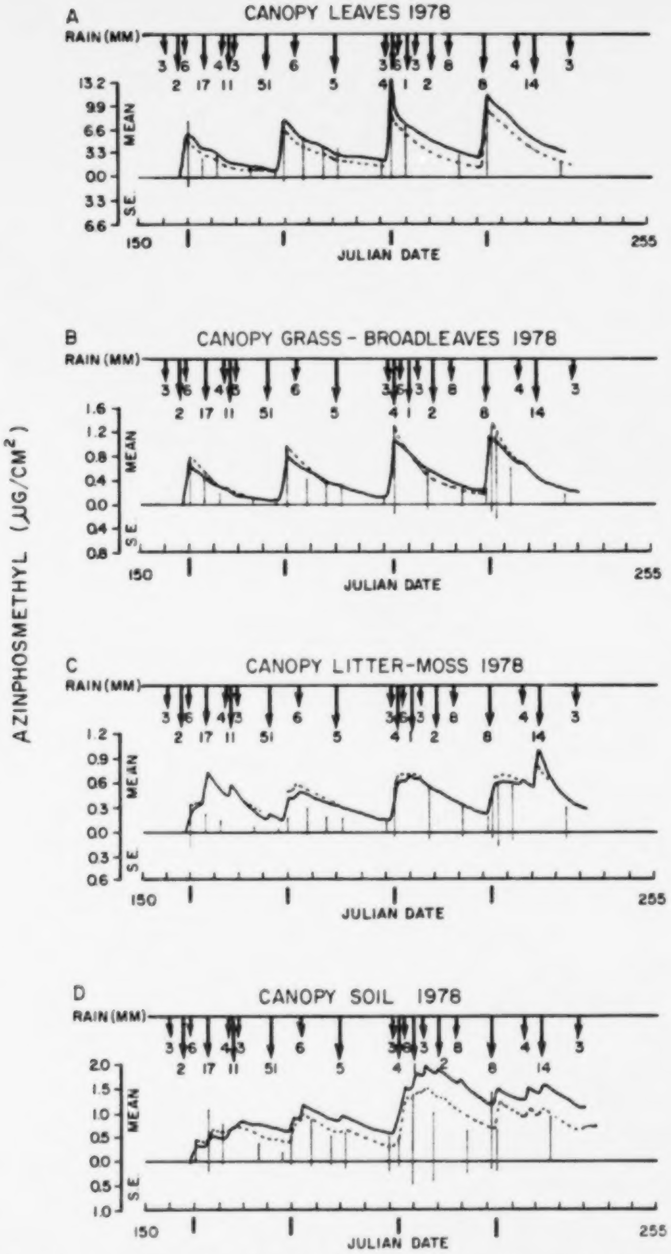


Figure II-8 (a-d) Actual and Predicted Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1978 Season, using predicted initial distribution for each spray period. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$ ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the residues using 1976 and 1977 data only, while the dashed line shows the predicted residues based on all three years (1976-1978) data.

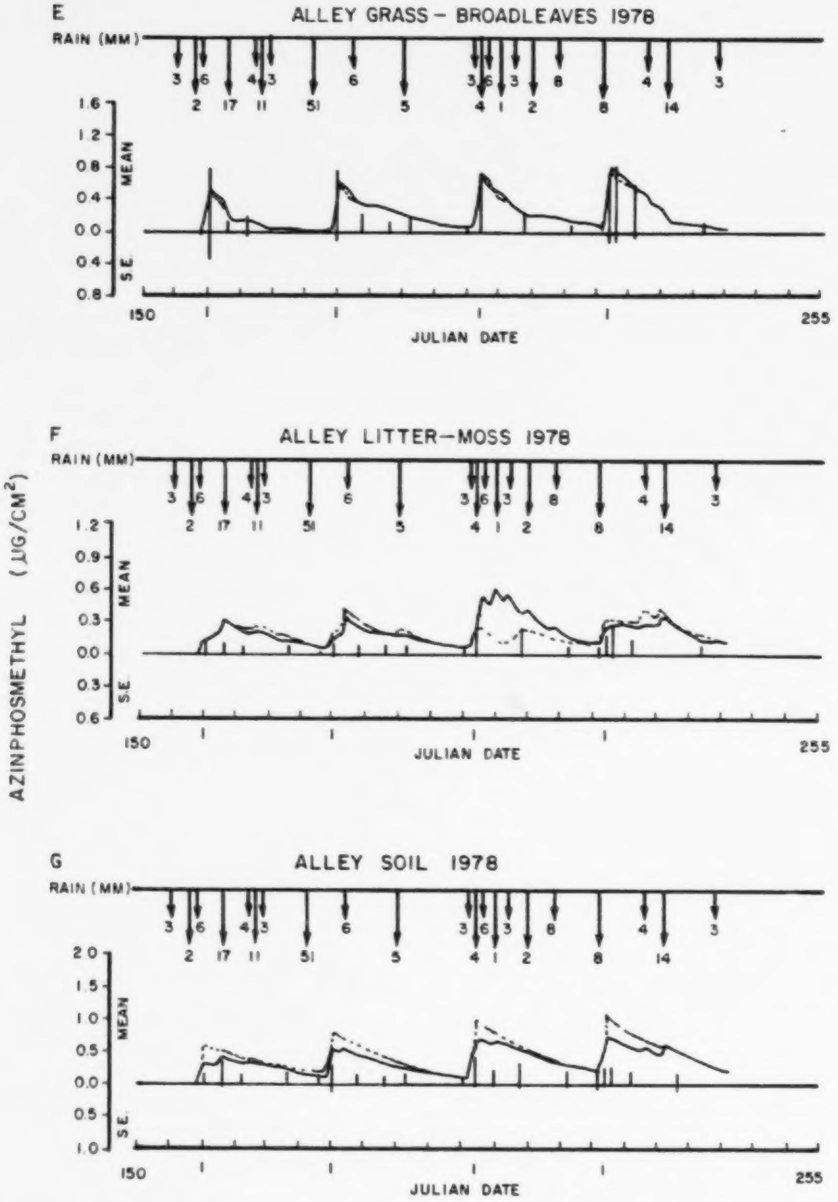


Figure II-8(e-g). Actual and Predicted Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1978 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (µg/cm^2 ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the change in residues using 1976 and 1977 data only, while the dashed line shows the predicted change in residues based on all three years' data.

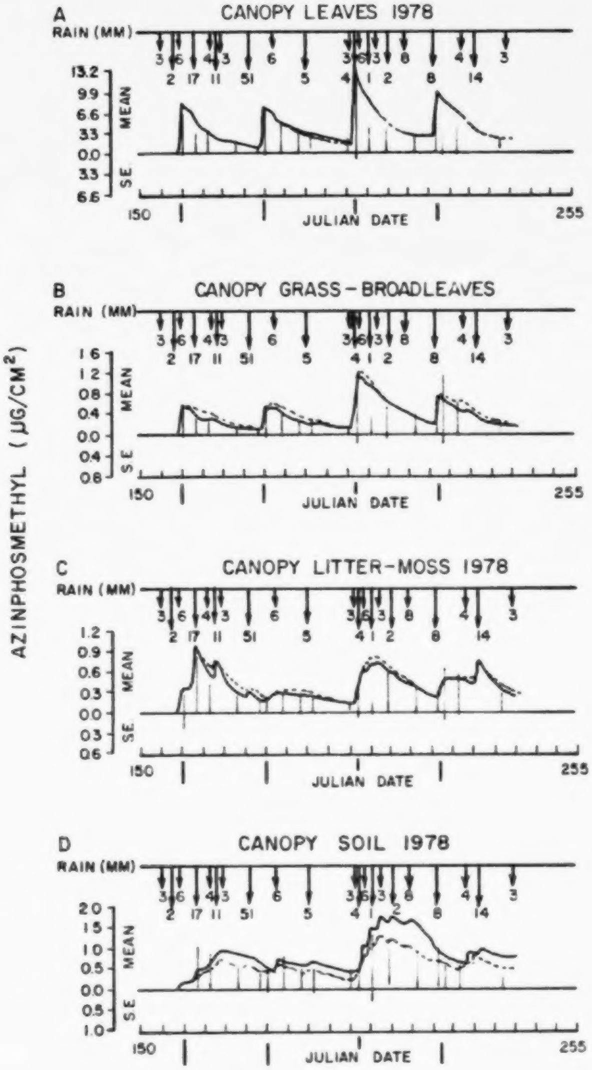


Figure II-9 (a-d) Actual and Predicted Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1978 Season, using the observed initial distribution for each spray period. Up ward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (μg/cm^2 ground area) is above the line and its corresponding standard error (S.E.) below the line. The line running through the bars represents the model's prediction of the residues using 1976 and 1977 data only, while the dashed line shows the predicted residues based on all three years (1976-1978) data.

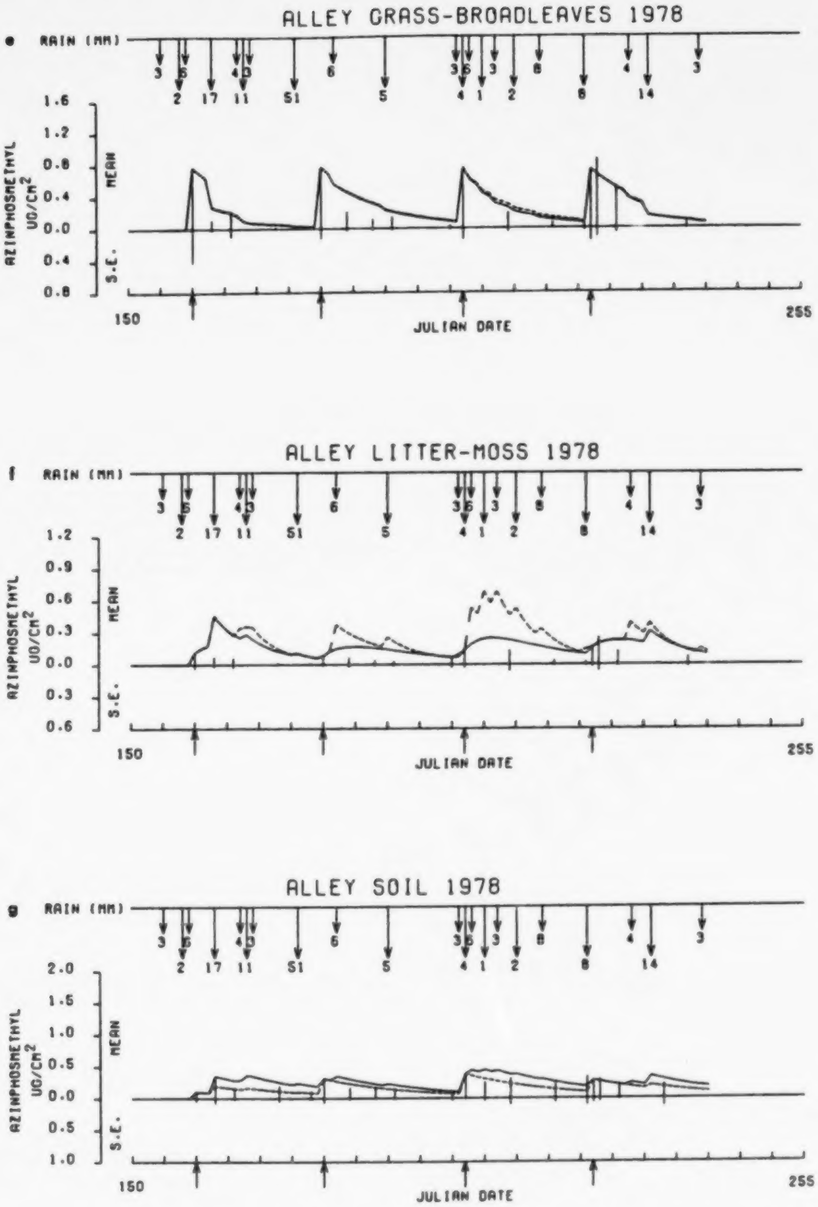


Figure II-9(e-g). Actual and Predicted Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1978 Season, Using the Observed Initial Distribution for Each Spray Period. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$ ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the residues using 1976 and 1977 data only, while the dashed line shows the predicted residues based on all three years' (1976-1978) data.

It is often difficult to determine an appropriate criterion for goodness of fit of model predictions to field determined values. In this study, the heterogeneity of the samples, lack of uniformity of application, variation in the microclimate, and other factors combined to yield large errors in residue estimates. In Table II-1, column 3 indicates the root mean square error (RMSE) of the daily mean for each layer from the values on which it is based. Clearly no model prediction could be expected to have a smaller RMSE from the measured residue values than the RMSE for the means shown in column 3.

Validation of the model is most convincingly demonstrated by comparing model predictions with a set of data which were not used in model parameterization. Therefore, for this purpose the movement and attenuation model was parameterized with 1976 and 1977 data only. In column 1 model predictions using these matrices together with 1978 application rates and environmental conditions are compared with measured 1978 field residues. Thus a comparison of column 1 with column 3 indicates the predictive performance of the model relative to the best possible prediction of each day's residue distribution. Model predictions based on matrices parameterized with data from all three seasons (1976-1978) are not independent of the 1978 residue data being used for model validation (see Figures II-4, II-5, II-6, II-7). However, these matrices are still of interest as our best estimate of the orchard residue dynamics. Column 2 shows RMSE's between measured 1978 field residues and predictions based on these matrices together with 1978 application rates and environmental conditions.

Comparison of the RMSE's in column 3 of Table II-1 shows the expected direct relationship of RMSE to sample mean. The similarity of the RMSE's in columns 1 and 2 indicate little difference in the predictive capability of the matrices, based on 1976 and 1977 data, with or without the 1978 data. Comparison of columns 1 and 2 with column 3 shows the best fit of the predicted values was in the Grass-Broadleaf layer. The RMSE's for this layer averaged 14% greater than the mean RMSE for both predictions. The RMSE's for the canopy litter-moss layer, based on both predictions, averaged 24% and the canopy soil averaged 22% greater than the mean RMSE, while the tree layer RMSE based on both predictions averaged 21% greater than the mean RMSE for this layer. The poorest fit was in the Alley litter-moss and soil layers. RMSE's for these layers based on predicted values averaged well over 100% greater than the mean RMSE. This may be due to the greater heterogeneity in composition of the alley litter-moss layer and low residue levels distributed to these layers.

The accuracy with which the model predicts post-deposition residue movement and attenuation is partially masked by the errors in prediction of initial distribution and drift. While sophisticated drift models can be developed, the parameterization of these models for a particular field situation requires an intensive measurement effort. For some spray applications, our simple drift model, based on limited measurements of drift, caused predicted residue levels on spray days to differ considerably from the measured levels. These differences affect the model's accuracy throughout the remainder of the season. In order to eliminate the effects of drift and to better evaluate the model's ability to track residue movement and attenuation, a separate test of the model was made. In this test, on each day of spray application, the residue distribution in the model was set to the distribution observed in the field on that day. The model then was used to predict only the subsequent residue attenuation and movement. Figures II-9(a-g) shows these predicted residues versus the measured values for 1978, in the same format as

TABLE II-1. COMPARISON OF THE MODEL PREDICTIONS (INCLUDING DRIFT)[a] WITH AZINPHOSMETHYL RESIDUE DATA FOR THE 1978 SEASON

Region	Layer	Root Mean Squared Error[b] From Sampled 1978 Residue Data			
		1 1976-1977 Prediction Matrices	2 1976-1978 Prediction Matrices	3 1978 RMSE'S Daily Mean	Sample Size
Canopy	Leaves	2.699	2.387	2.102	164
	Grass-broadleaves	0.327	0.290	0.262	131
	Litter-moss	0.300	0.293	0.239	136
	Soil	0.740	0.832	0.642	114
Alley	Grass-broadleaves	0.253	0.249	0.228	122
	Litter-moss	0.148	0.126	0.017	144
	Soil	0.480	0.338	0.130	105

[b] Mean squared errors for the relationship between the predicted and sample values shown in figures 6a-6g. Column 1 shows the relationship of the 1978 data to the model parameterized with data from 1976-1977, while column 2 shows the 1978 data versus the model parameterized with 1976-1978 data. Column 3 shows the root mean squared error determined for the individual 1978 samples about each sample day's mean.

[a] Spray distribution was predicted using a model for drift and deposition. Therefore errors in drift prediction effect the RMSE values shown..

Figures II-8 (a-g). In Table II-2, the fit of the predictions to the measured residues is quantified. As in Table II-1, column 3 shows the root mean square errors of the daily mean for each layer from the values on which it is based. The sample numbers and most means are lower than in Table II-1 because the spray date measurements have been excluded. Columns 1 and 2 in Table II-2 are analogous to those columns in Table II-1, with the errors due to initial spray distribution and drift eliminated.

Comparison of columns 1 and 2 with column 3 in Table II-2 shows the best fit of the prdicted values was in the soil layer. The RMSE's for this layer averaged 17% greater than the mean RMSE for both predictions. The RMSE's for the grass-broadleaf layer, based on both predictions, averaged 25% greater than the mean RMSE, while the tree leaf layer RMSE based on both predictions averaged 39% greater than the mean RMSE for this layer. The poorest fit was in the litter-moss layer. RMSE's for this layer based on predicted values averaged 61% greater than the mean RMSE for the canopy region, and well over 100% greater than the mean RMSE for the alley region. Again, this may be due to the greater heterogeneity in composition and low residue levels distributed to this layer.

The effects of rainfall on the model predictions are quite striking. In some layers a net movement out is seen while in others more pesticide is carried in. Of major importance is the fact that throughout the season the residues in the tree are continually redistributed to the orchard floor. This movement counteracts the attenuation mechanisms, resulting in a slower net loss rate of pesticide and, in some situations, a net increase in residue deposits to layers of the orchard floor. Such information on pesticide dynamics within the orchard ecosystem has in the past been given little consideration in assessing crop protection. Some pest species of apples and some of their natural enemies have life stages which inhabit the orchard floor, subjecting those populations to the pesticide residue dynamics of these layers. More information is needed on the possible impacts of pesticides on these populations and their interactions. Future pest management strategies, involving the integration of chemical control techniques with biological, cultural, and other control measures, must consider pesticide fate throughout the entire orchard ecosystem.

Although the estimation of pesticide fate is an end in itself, the overall goal of this research was to model the effect of azinphosmehtyl on ground dwelling invertebrates which inhabit the orchard. Field studies conducted concurrently within the same orchard, along with laboratory data, collected on the isopod Trachelipus rathkei (Snider, 1979; Snider and Shaddy, 1980), were used to develop a model describing its ecobiology and temporally distributed mortality (See Chapter X and Goodman, 1982). A form of the fate model presented here was used to determine the time-course of azinphosmethyl exposure.

The model in the form reported here predicts azinphosmethyl redistribution and attenuation as a function of time and rainfall data only. In order to account for the effects of other environmental factors on pesticide dynamics, a more sophisticated model is required. Further model development should involve the decomposition of both the movement and attenuation matrices to represent their component physical, chemical, and biological processes, each a function of the relevant environmental variables (see Chapters III and IV). This decomposition requires controlled experiments, many of which can only be performed in a laboratory setting. However, the data and parameters reported here remain as a set of field measurements against which such lab studies may be compared or calibrated.

TABLE II-2. COMPARISON OF THE MODEL PREDICTIONS (EXCLUDING SPRAY DATES)[a] WITH AZINPHOSMETHYL RESIDUE DATA FOR THE 1978 SEASON

Region	Layer	Root Mean Squared Error[b] From Sampled 1978 Residue Data			
		1 1976-1977 Prediction Matrices	2 1976-1978 Prediction Matrices	3 1978 RMSE's Daily Means	Sample Size
Canopy	Leaves	2.699	2.387	2.102	164
	Grass-broadleaves	0.327	0.290	0.262	131
	Litter-moss	0.300	0.293	0.239	136
	Soil	0.740	0.832	0.642	114
Alley	Grass-broadleaves	0.253	0.249	0.228	122
	Litter-moss	0.148	0.126	0.017	144
	Soil	0.480	0.338	0.130	105

[b] Mean squared errors for the relationship between the predicted and sample values shown in the figures 6a-6g. Column 1 shows the relationship of the 1978 data to the model parameterized with data from 1976-1977, while column 2 shows the 1978 data versus the model parameteized with 1976-1978 data. Column 3 shows the root mean squared error determined for the individual 1978 samples about each sample day's mean.

[a] To better evaluate the model's ability to track residue attenuation and movement and to eliminate the error associated with drift estimates. The residue distribution was set to the measured values after each spray. Therefore spray dates were excluded in the calculation of RMSES's.

CHAPTER III

AIRBORNE LOSS FROM THE ORCHARD

INTRODUCTION

Recent field studies have indicated that airborne loss plays a major role in the attenuation of field-applied pesticide residues (Taylor et al., 1976; Taylor et al., 1977; White et al., 1977; Woodrow et al., 1977; Claith et al., 1980). Taylor et al. (1977) report that attenuation of dieldrin applied to orchard grass was due solely to volatilization. In-depth reviews of both laboratory and field studies have been prepared by Spencer et al. (1973) and Spencer and Claith (1975, 1977). Volatilization of pesticides under field conditions is discussed by Taylor (1978). Techniques for measuring volatilization rates in the field are described by Caro et al. (1971) and Parmele et al. (1972). Orchard sampling of airborne pesticides bas been for the most part limited to studies of worker re-entry inhalation or dermal contact with airborne residues (Iwata et al., 1977; Gunther et al., 1977).

Airborne loss consists of spray droplet drift, evaporation and volatilization at application, and post-application losses by volatilization and wind erosion (Ebling, 1963; Leonard et al., 1976). The work described here was designed to assess the contribution of airborne loss to the overall attenuation of the organophosphate insecticide azinphosmethyl, 0,0 dimethyl-S-(4-oxo-1, 2,3, benzotriazin-3(4h)-ylmethyl) phosphorodithioate (Guthion), in a Michigan apple orchard ecosystem. Previous field work (Chapter I) designed to estimate the distribution, attenuation, and movement of azinphosmethyl in a deciduous orchard environment suggested that airborne loss was the major pathway of pesticide attenuation soon after application. In the present study airborne residues of azinphosmethyl were measured directly, accompanied by meteorological data, over a season of periodic low-volume spray applications. These measurements along with orchard deposit residue data were used to estimate pesticide airborne flux from the orchard as a part of the total attenuation of pesticides over the season.

ANALYTICAL METHODS

Procedures for the residue analysis of all sample types are described in Chapter I. Briefly, dislodgeable residues were determined by the procedure of Gunther et al. (1973), surface-penetrated residues procedure of Steffens and Wieneke (1976), and soil residues by the procedure of Schulz et al. (1970). Targets, consisting of two circles of Whatman No. 1 paper, 18.5 cm diameter (attached one atop the other by a single staple to a cardboard backing), were extracted for two hours in a soxhlet extractor using a mixture of hexane: acetone, 100 ml:25 ml.

Airborne Residues. The porous polyurethane foam (PPF) plugs (ester form), five cm long and 4.5 cm in diameter, were used as the trapping medium for sampling azinphosmethyl airborne residues. The PPF plugs were rinsed with distilled, deionized water in a Nalgene pipet washer for six hours followed by soxhlet extraction with 500 ml acetone for six hours and then 500 ml hexane for six hours prior to use. This method is similar to that used by Turner and Glotfelty (1977). After sampling, the PPF plugs were soxhlet extracted for four hours with 500 ml of a 4:1 hexane-acetone solution. Extracts were further concentrated by rotary evaporation followed by air evaporation prior to analysis by GLC.

Trapping ability and extraction procedures were tested in the laboratory. A closed glass system consisting of a volatilizing chamber (U-tube) followed by two plugs in series, followed by a cold trap (dry ice in acetone) was used. Air flow was drawn at 1.0 m^3/hr for 60 minutes. At this flow no pressure drop could be measured with a mercury barometer. No azinphosmethyl was found in the second plug or the cold trap (limit of detection was 1.0 ng). Recovery and standard deviation was 91.7 ± 1.6 % from the volatilization of 42.8 ± 13 μg(three repetitions). The detection limit for azinphosmethyl in air was approximately .01μg/m^3.

Quantitation of azinphosmethyl was accomplished using a Tracor 560 gas chromatograph having a flame photometric detector in the phosphorus mode. A six-foot glass column (2 mm i.d.) packed with 3% SE-30 on Gas Chrom Q, 60/80 mesh, was operated at 195 C;N_2, 40 ml/min; air, 90 ml/min; H_2, 60 ml/min. This system was interfaced with a digital PDP 11/20 RSTS computer for integration of the area under the single peak produced.

EXPERIMENTAL SITE AND PESTICIDE APPLICATION

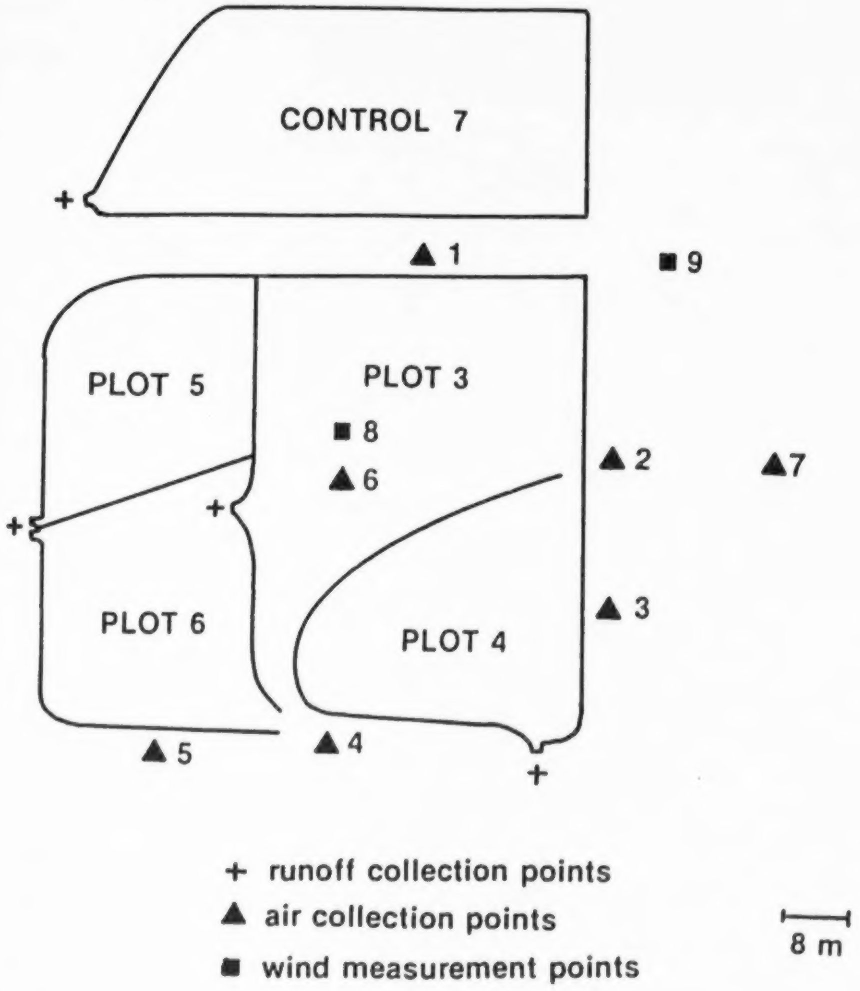
The apple orchard was located in the vicinity of Grand Rapids, Michigan in Kent County. The 12 one-year old trees were a mixture of semi-dwarf duchess and wealthy cultivars. In the spring of 1976, the orchard received a moderate pruning and cleaning to counter several years of disuse. The orchard plan was mowed to a height of approximately 5 cm prior to the first, second, and third spray applications. Four experimental plots and one control plot (Figure III-1) were established by a method designed to facilitate the study of azinphosmethyl loss via surface runoff study conducted in 1977 are reported in Chapter I.

Azinphosmethyl (Guthion^R, 50% W.P., Mobay Chemical Company) was applied with a custom-built, low pressure, low volume sprayer similar to one developed by Howitt and Pshea (1965). The across plot average application rates and standard deviations (Kg ha^{-1}, 50% w.p. 100ℓ^{-1} ha^{-1}) were 1.3 ± 0.2 on June 9, 1.6 ± 0.6 on June 29, 1.0 on July 21, and 1.6 ± 0.2 on August 10. A more detailed description of the experimental site, sprayer design, and application techniques can be found in Chapter I.

SPATIAL STRUCTURE OF THE ORCHARD

The orchard plots were subdivided both vertically and horizontally. Horizontally, each plot was subdivided into four regions potentially different with respect to initial pesticide distribution (see Figure III-2). Region 4 (under the canopy) was determined to be 32% of the area in plot 1, 34% in plot 2, 54% in plot 3, and 45% in plot 4. The remainder of the plot was divided among the three alley regions in a ratio of 2:3:1 for plots 1 and 2, and 1:2:1 for plots 3 and 4. The difference in the ratios was due to the closer spacing of the rows along the North-South axis in plots 3 and 4. The number of trees was 24 in plot 1, 15 in plot 2, 10 in plot 3, and 11 in plot 4. Tree heights averaged 3.0 meters. Vertically, each alley region was divided into three compartments; grass-broadleaves, litter-moss, and soil.

Figure III-1. Orchard Plots Showing Air Sampling Locations


CONTROL 7
PLOT 5
PLOT 3
PLOT 6
PLOT 4
▲ 1
■ 9
■ 8
▲ 6
▲ 2
▲7
▲ 3
▲ 5
▲ 4
+ runoff collection points
▲ air collection points
■ wind measurement points
8 m

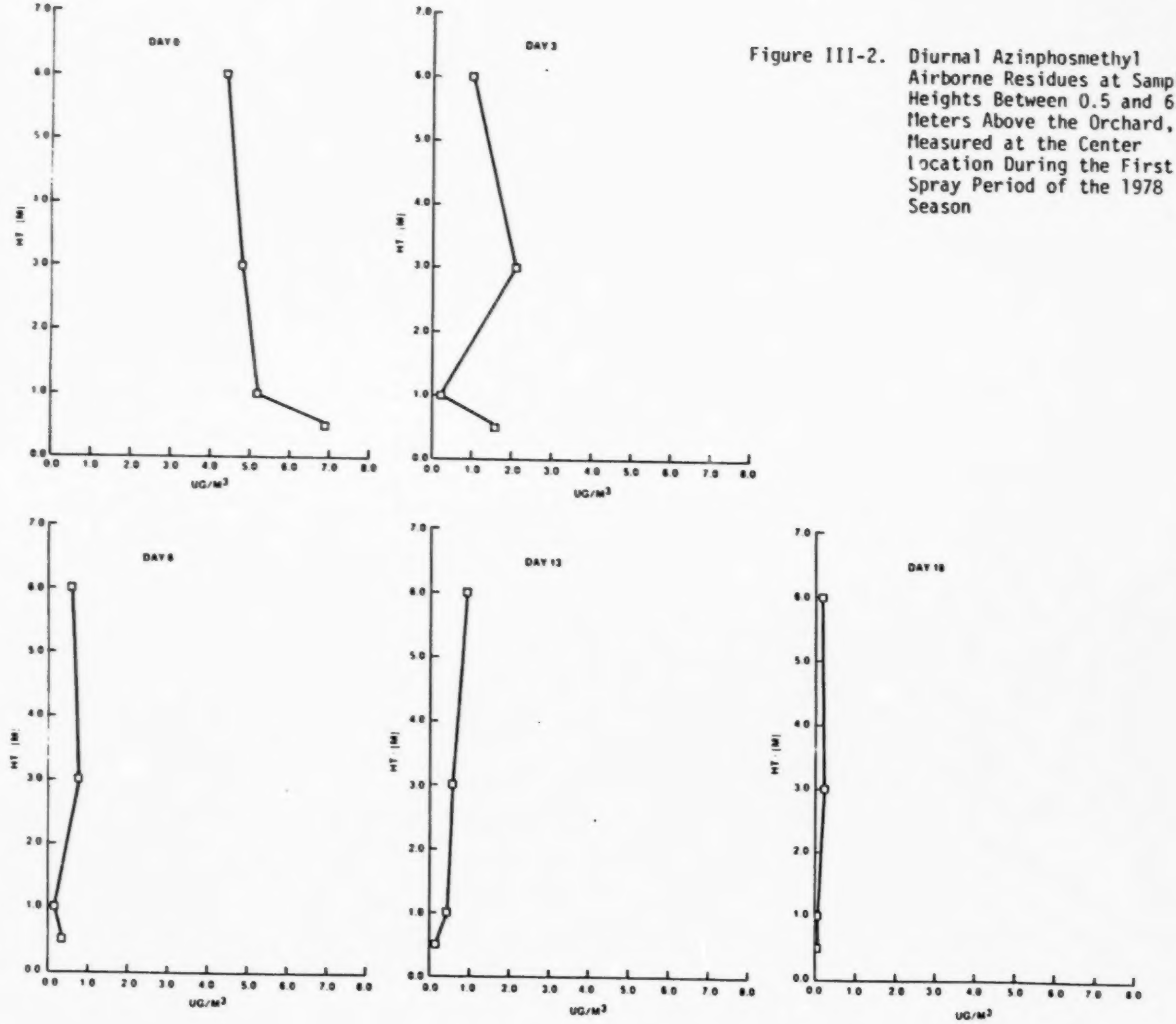


Figure III-2. Diurnal Azinphosmethyl Airborne Residues at Sampling Heights Between 0.5 and 6.0 Meters Above the Orchard, Measured at the Center location During the First Spray Period of the 1978 Season

ORCHARD SAMPLING PROCEDURES

Deposit residue sampling was carried out in a manner similar to the two previous seasons, as described in Chapter I. An abbreviated description of sampling procedures is given here. To determine azinphosmethyl initial horizontal distribution, a series of 15 to 20 ground-located, filter paper targets was deployed among the four regions (Figure III-2) in each plot prior to application. Targets were placed in the center of the alley regions and at the in-row mid point between the tree trunk and the edge of the canopy region. The distribution of azinphosmethyl residues was also determined for the trees and among the three ground layers (grass-broadleaves, litter-moss, soil). In each plot, three trees were sampled and four samples of each ground layer were taken, two from the canopy and two from the alley regions. Trees were subdivided for sampling into lower (1-2) and upper (2-3 m) regions. Tree heights averaged 3 m. Thirty to 35 leaf discs were taken per sample. Block sampling was employed for both ground samples and trees. One-half m^2 ground area sites and trees were selected randomely for consecutive sampling in the first and second spray periods; areas at the end of rows and close to adjacent plots were avoided. Similarly, new sites were chosen for consecutive sampling during the third and fourth spray periods. Plots were sampled in sequence, between 1300 and 1500 hr at various times following application, as shown in Table III-1.

AIRBORNE RESIDUE SAMPLES

Two air sampling masts were employed, one located at the center of the sprayed plots and one at the downwind edge (Figure III-1). The PPF plugs were positioned in glass cylinders, tapered at one end, and located at heights of 0.5, 1.0, 3.0 and 6.0 meters above the orchard floor. Air was drawn through each plug at a rate of 8.33ℓ/minute giving a combined flow rate of 33.33ℓ/minute measured by flowmeter, controlled by an adjustable needle valve. Flow rate was maintained with an electric vacuum pump powered by a gas generator. On June 9 the orchard air was sampled during application at the downwind edge (Location 2, Figure III-1) and also at Location 1, as the wind direction had a slight northern component. Samples were taken from 0700 to 1000. During the June 29 application samples were taken at the downwind edge (Location 2) and 20 meters from the downwind edge (Location 7). The two remaining spray applications (July 21, August 10) were sampled at the downwind edge only. The orchard air was sampled in the afternoon following each application and on successive dates for two hours, between 1300 and 1500 (see Table III-1). Wind speed was measured at three meters (Location 12) during application and at three and six meters (Location 13) during afternoon sampling periods. Wind direction was continuously recorded from a wind vane mounted on the same mast. Additional measurements of temperature, humidity, solar radiation, and rainfall were continuously recorded throughout the season (Location 9). Rainfall amounts and wind speed data are included in the summary of significant events for the 1978 season shown in Table III-1. Temperature and humidity data are shown in Figures III-7 and III-8.

RESULTS AND DISCUSSION

Table III-2 shows the results of the analysis of targets for the first spray day of the 1978 season. The average amount is express in $\mu g/cm^2$ ground area and proportions shown are proportions of the dose applied to each plot.

Table III-1. Summary of Significant Events for the Orchard, 1978 Season

Spray Date	Sample Date	Days Since Spray	Rainfall Date	Rainfall Amount (mm)	Windspeeds^{a} (m/s) during Air Sampling 3 m	6 m
			Orchard Mowed 1 June			
			7 June	2.0		
			8 June	6.1		
9 June	9 June	0			2.4^{c}, 2.2^{d}	4.4
	12 June	3	12 June ^{b}	17.3	2.7	4.5
	15 June	6			1.6	3.9
			16 June	3.6		
			17 June	11.2		
			18 June	3.0		
	22 June	13			1.3	2.2
			25 June	51.3		
	27 June	18			1.6	2.1
			Orchard Mowed 28 June			
29 June	29 June	0			e	e
			1 July	5.6		
	3 July	4			1.3	2.0
	7 July	8				
	10 July	11	9 July	5.1	2.1	3.6
	19 July	20			0.9	2.2

Table III-1 continued

Spray Date	Sample Date	Days Since Spray	Rainfall Date	Rainfall Amount (mm)	Windspeeds[a] (m/s) during Air Sampling	
			Orchard Mowed 20 July			
			20 July	3.0		
21 July	21 July	0	21 July[b]	4.3	[f] N.D., 1.1[c]	N.D.[f]
			22 July	5.6		
	24 July 3		24 July[g]	0.8	0.5[d]	0.9
			26 July	3.0	N.D.[f]	N.D.[f]
	28 July	7				
			29 July	1.5		
			2 Aug	7.6		
	4 Aug	15			1.6	3.0
	9 Aug	20	9 Aug[b]	8.1	1.8	3.1[d]
10 Aug	10 Aug	0			0.7	1.3
	11 Aug	1			0.91	.3
	14 Aug	4			0.9	1.5
			16 Aug	3.6		
			19 Aug	14.2		
	21 Aug	11			0.7	0.9
	25 Aug	15			0.5	1.5

[a] Two hr mean, measured at 3 m and 6 m above the orchard floor (Figure 1, Location 6) between 1300 and 1500 hours.

[b] Rainfall occurred before sampling.

[c] Six hr mean, measured at 3 m above the orchard floor (Location 9) between 0600 and 1200 hours.

[d] Estimated value determined from the average ratio of wind speeds at 3.0 m and 6.0 m for the entire season and the wind speed measured for this date.

[e] Recorder malfunction

[f] None detected, limit of detection 0.5/ms.

[g] Rainfall occurred after sampling.

Figure III-7. Daily Temperature Range, 1978 Season

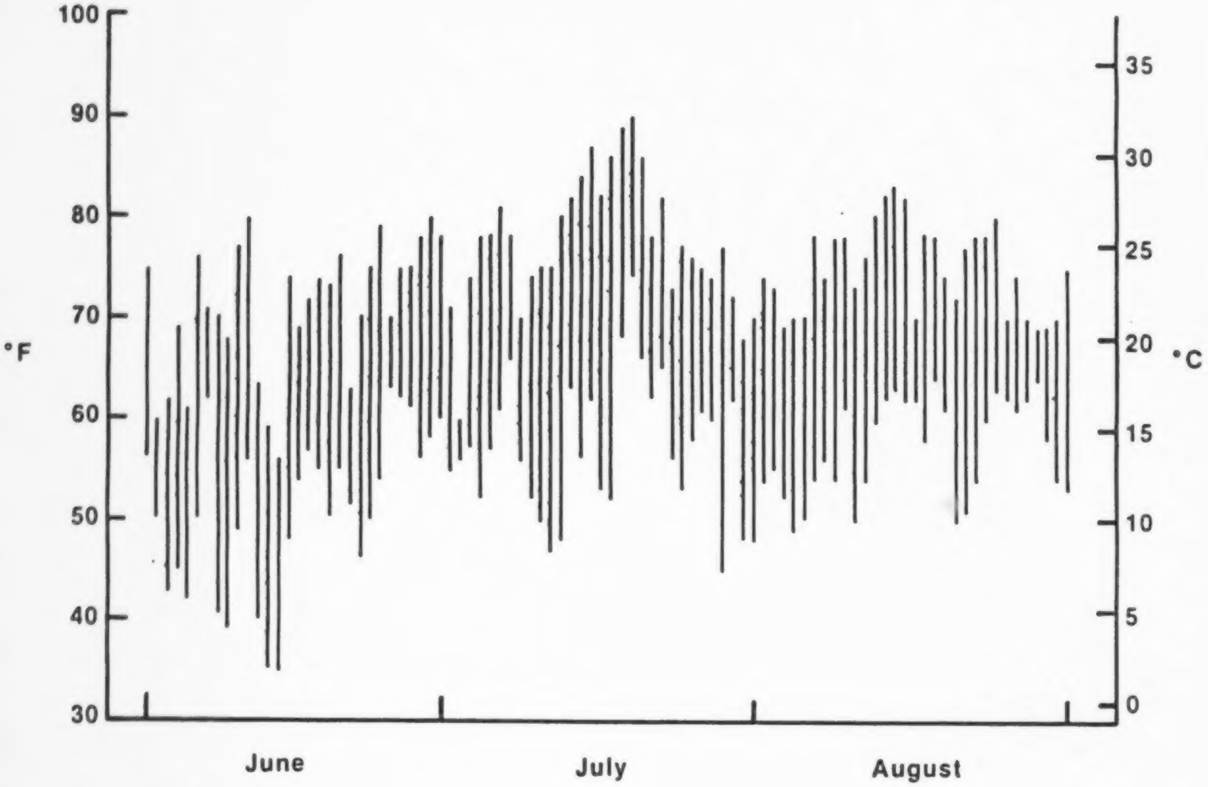


Figure III-8. Daily Minimum and Maximum Relative Humidity, 1978 Season

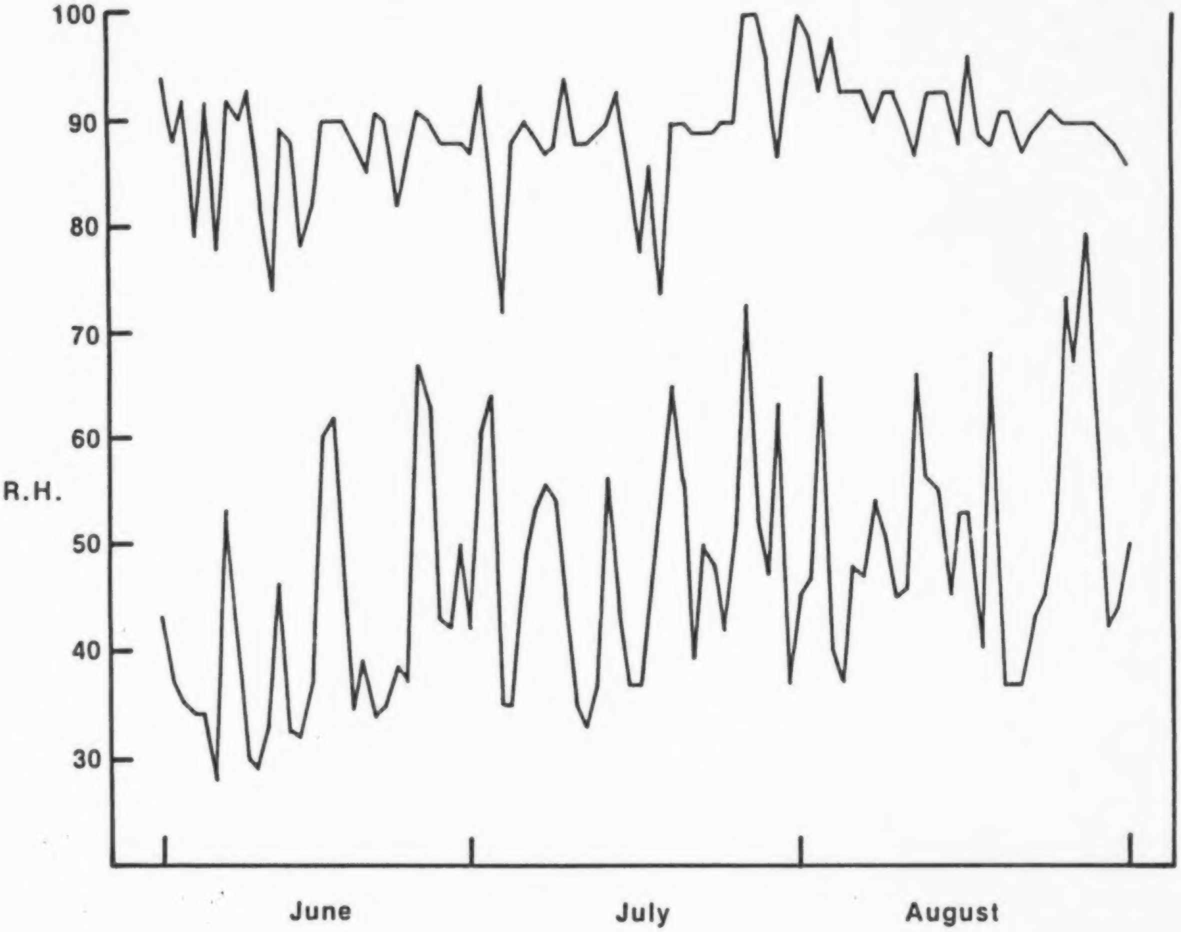


Table III-2. Azinphosmethyl Initial Horizontal Distribution from the Analysis of Targets, First Spray Period of the 1978 Season.

Plot		Alley(1)	Alley(2)	Alley(3)	Alley(4)
1	Average Amount (μg/cm^2 ± SE)	1.40 ± .15	1.16 ± .33	0.86 ± .27	1.04 ± .15
	Sample size	3.	3.	4.	4.
	Proportion	.052	.052	.010	.044
2	Average Amount (μg/cm^2 ± SE)	0.62 ± .16	1.37 ± .34	1.52 ± .25	1.09 ± .30
	Sample Size	3.	5.	4.	5.
	Proportion	.021	.096	.030	.081
3	Average Amount (μg/cm^2 ± SE)	1.09 ± .35	1.94 ± .28	0.95 ± .4	1.05 ± .35
	Sample Size	5.	4.	5.	3.
	Proportion	.018	.053	.014	.062
4	Average Amount (μg/cm^2 ± SE)	.018	1.24 ± .27	0.57 ± .15	1.07 ± .22
	Sample Size	1.	3.	6.	3.
	Proportion	.004	.059	.016	.094
Grand Average Amount (μg/cm^2 ± SE)		0.2 ± .27	1.431 ± .18	0.98 ± .20	1.06 ± .01

The grand average across plots shows that alley region 2 and the canopy region receive the majority of the residues reaching the ground. This agrees with the pesticide horizontal distribution data for the 1976 and 1977 seasons (Chapter I).

Vertical pesticide distribution for the first spray period of the 1978 season is given in Table III-3. The across plot average is represented by only two regions; alley and canopy. The average amounts for the alley represent weighted averages of alley regions 1, 2 and 3, weighted by % plot area. These data agree with the results of the 1976 and 1977 field studies in that the majority of the residues are initially distributed vertically to the tree leaves and the grass-broadleaves layer. Orchard soil received approximately 1.5% of the dose applied.

The vertical distribution of pesticide residues as proportion of dose applied is shown in Table III-4. Proportions were determined from the dose applied to each plot and then averaged. Tree surface area was estimated as 460,000 cm^2/tree (see Chapter I). The proportion of the pesticide applied that was distributed as surface penetrated residues was estimated from matched samples from the first spray day of the 1978 season. The surface-penetrated to total dislodgeable residue ratios and standard errors were determined as follows: leaves, .081 ± .015; grass-broadleaves, .190 ± .002; litter, .421 ± .078; moss, .272. These ratios were multipled by the appropriate dislodgeable residue proportions to estimate the surface-penetrated proportion. Soil residues were determined on a whole sample basis. Summing all dislodgeable, surface-penetrated and soil residue proportions for the first spray day of 1978, across both alley and canopy regions, yielded the estimate that 72.1% of the pesticide applied was initially deposited in the various orchard strata. This estimate is considerably higher than the 1977 estimate of 55.6%. The 1976 estimate was 66.1% (Chapter I). These are only crude estimates which, after accounting for extraction efficiency, assume that all residues in the samples analyzed were accounted for (a more detailed discussion of the point can be found in Chapter I). The most likely sources of error are: (1) underestimation of the amount applied and (2) uneven application (due to steep slope in plot 4) and sampling not representative of residue levels present. The estimated proportion of pesticide applied initially distributed to the trees in plot 4 for the first spray of the 1976 season was also greater than the estimates for the other plots resulting in a total deposit estimate of 84.6% of the dose applied for that plot. The 1977 data shows no great variation in tree proportion (31.5%, S.D., 6.2%) among plots.

On the premise that all the residues deposited in the orchard were accounted for, 27.0% of the dose applied to the orchard in the first spray period of the 1978 season is assumed to be airborne loss, primarily as drift at application, but also as volatilization and wind erosion in the four hours between application and sampling. Table III-5 shows estimates by plot of airborne loss using target data to determine proportion distributed to the orchard floor. The across-plot average airborne loss estimate of 26.7% is in close agreement with the estimate made using the orchard floor deposit residue samples.

Azinphosmethyl concentrations in the air measured during application at sampling heights between 0.5 meters and 6.0 meters above the orchard floor are given in Table III-6. For those samples taken at the downwind edge, concentrations measured are roughly uniform from 0.5 to 6.0 meters. Differences in mean amounts sampled between the four spray dates are thought to be primarily a function of wind speed. Temperature and relative humidity (R.H.) also determine the amount of pesticide reaching the downwind edge sampling

Table III-3. Initial Vertical Distribution of Azinphosmethyl Dislodgeable Residues,[a] First Spray Period of the 1978 Season[b]

	Leaves		Grass-Broadleaves	Litter-Moss	Soil
	Upper	Lower			
Canopy					
Average Amount ($\mu g/cm^2 \underline{+}SE$)	1.69 ± .17	4.64 ± .71	0.59 ± .03	0.11 ± .05	0.21 + .04
Sample Size	11	12	4	6	8
Alley					
Average Amount ($\mu g/cm^2 \underline{+}SE$)			1.00 ± .56	0.12 ± .04	0.09 ± .05
Sample Size			4	7	5

---

[a] Except soil residues which were determined on a whole sample basis.

[b] Across plot average and standard errors expressed as $\mu g/cm^2$ ground area, except tree leaves which are $\mu g/cm^2$ leaf area. Lower (1-2m) and upper (2-3m) regions of the tree were sampled separately.

Table III-4. Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied (± S.E.) from the Analysis of Samples for the First Spray Period of the 1978 Season.

	Alley		Canopy		
	Dislodgeable	Surface-Penetrated	Dislodgeable	Surface-Penetrated	Total
Tree			.513 ± .093	.036	
Grass-Broadleaves	.077 ± .036	.015	.028 ± .002	.005	.721 ± .100
Litter-Moss	.009 ± .002	.004	.008 ± .003		
Soil	.009 ± .005		.014 ± .004		

Table III-5. Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied, Using Target Data to Calculate the Proportion Reaching the Orchard Floor, for the First Spray Period of the 1978 Season.

	Orchard Floor		Tree		
Plot	Alley	Canopy	Dislodgeable	Surface-Penetrated	Total
1	.114	.044	.391	.028	.607
2	.147	.081	.483	.029	.670
3	.085	.061	.549	.032	.637
4	.079	.094	.789	.056	1.018
					.733 ± .096

Table III-6. Azinphosmethyl Concentrations ($\mu g/m^3$) at Sampling Heights between 0.5 and Six Meters Over Orchard.

Date	Days Since Spray	Center				Location[a]	Downwind Edge				Location[a]
		Height Above Orchard Floor									
		0.5	1	3	6		0.5	1	3	6	
9 June[b]							17.70	27.70	29.30	22.80	2
9 June[b]							12.70	3.40	15.80	15.10	1
9 June	0	6.90	5.20	4.80	4.40	6	5.70	4.60	4.40	5.30	2
12 June	3	1.58	0.23	2.10	1.00	6	0.35	0.92	2.40	1.13	4
15 June	6	0.36	0.17	0.78	0.59	6	0.13	0.09	1.47	0.80	1
22 June	13	0.17	0.44	0.37	0.93	6	0.07	0.13	0.27	0.31	1
27 June	18	0.07	0.07	0.23	0.17	6	0.05	N.D.[c]	0.29		2
29 June[b]							26.40	25.00	24.10	27.60	2
29 June[b]							6.67	7.69	27.70	9.54	7
29 June	0	1.00	1.92	2.88	1.38	6	1.94	2.53	0.91	0.64	2
3 July	4	1.55	1.26	0.35	0.67	6	1.77	.96	0.59	2.30	5
10 July	11	0.09	0.62			6	0.32	0.24	1.00	0.05	3
19 July	20	0.17	0.11	0.11	0.22	6	0.25	1.14	0.11	0.16	2
21 July[b]							11.82	18.18	18.18	13.33	1
21 July	0	1.02	0.19	0.57	0.82	6	1.30	1.51	0.87	1.15	1
24 July	3	0.63	0.35	0.91	0.38	6	0.36	0.38	0.35	0.53	1
28 July	7	0.23	0.09	0.22	0.16	6	0.13			0.25	2
4 Aug	15	0.09	0.05	0.05	0.09	6	0.16	0.32	0.28	0.25	3
9 Aug	20	0.06	0.21	0.14	0.22	6	0.57	0.09	0.07	0.10	1
10 Aug[b]							14.06	15.22	18.33	16.67	4
10 Aug	0	0.86	1.29	3.13	0.95	6	0.57	0.27	0.43	0.25	3
11 Aug	1						0.73	0.40	0.61		2
14 Aug	4						0.34	0.70	0.77		2
21 Aug	11						0.32		0.67		2
25 Aug	15		0.22			6					

[a] Location of sites shown in Figure 1.

[b] Azinphosmethyl concentrations measured during application, all others are 2 hr mean sample concentrations taken between 1300 and 1500 hours.

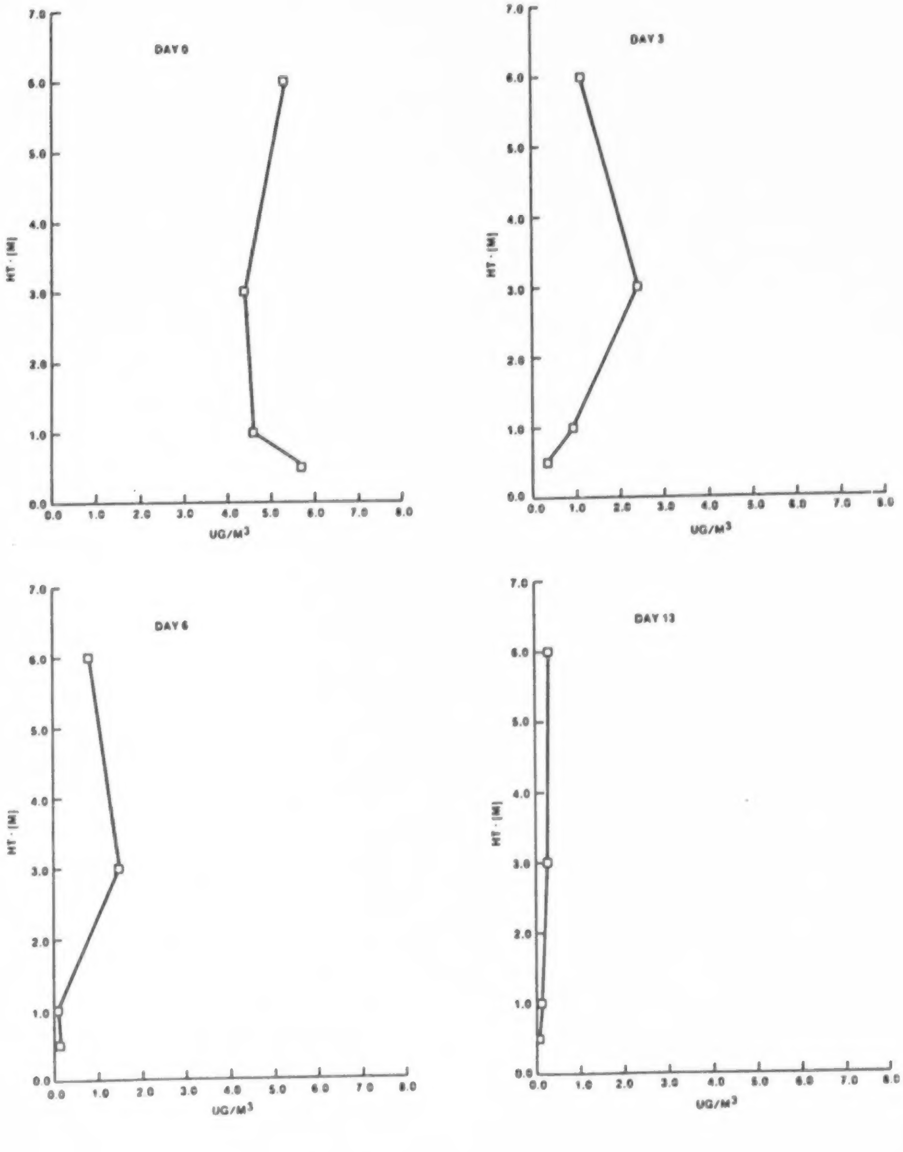
[c] None detected, limit of detection .01 $\mu g/m^3$.

sites. Conditions favoring rapid evaporation tend to reduce the droplet spectrum towards smaller droplets which travel farther before being deposited out. Temperature, through its effect on atmospheric conditions, also influences spray drift. Inversion conditions favor a smaller drift cloud by discouraging vertical diffusion. Turbulent atmospheric conditions accelerate both vertical and lateral dissipation of spray droplets (Yates and Akesson, 1973; Maybank and Yoshida, 1977). The mean pesticide concentration measured during application on June 9 was 22.9 μg/m^3. The mean wind speed at 3.0 meters was 2.2 m/s. The temperature ranged from 3.9°C (0600) to 11.9°C (1200) and the R. H. ranged from 92% (0600) to 35% (1200). On July 21 the mean pesticide concentration measured during application was 15.4 μg/m^3. The mean wind speed measured at 3.0 meters during sampling was 1.1 m/s. The temperature ranged from 17.2°C (0600) to 18.4°C (1200) and the R. H. ranged from 89% (0600) to 78% (1200). Comparison of wind speeds between these two dates suggests that the higher wind speed during application on June 9 was responsible for the higher concentrations measured at the downwind edge. If the airborne pesticide concentrations measured during application on these two dates are scaled by the average amount of pesticide applied the difference is more pronounced.

On June 29 a second mast was located 20 meters from the downwind edge. Air samples taken during application indicated that there was rapid dissipation of airborne residues between the two masts at all heights except 3.0 meters. This persistence at 3.0 meters may be the result of pesticide moving through the air as a plume generated by the closer passes of the sprayer.

Table III-6 also shows azinphosmethyl concentrations in air at sampling heights between 0.5 meters and 6.0 meters over the orchard at two locations; the center of the sprayed plots (Figure III-1, Location 6) and at the downwind edge. Samples were taken between 1300 and 1500 hr on the day of application and on selected days following application (Table III-1). Mean wind velocities at 3.0 and 6.0 meters for the two-hour sampling period are also given in Table III-1. Graphical representation of airborne pesticide residues for the first spray period is shown in Figures III-2 and III-3. These figures show a systematic decline in airborne pesticide residues at all heights above the orchard floor over the 18-day sample period. Data for the remaining spray periods (Table III-6) also show this trend. As might be expected, the decline in airborne pesticide residues agrees fairly closely with the decline in orchard deposit pesticide residues (Figure III-4). Variation in airborne pesticide residues between the heights sampled is the greatest on the early sample days following application, with the highest airborne pesticide at 0.5 meters the day of application (day 0) and at 3.0 meters 3 and 6 days following application. Lower levels of azinphosmethyl airborne residues were measured in the afternoon of the second, third, and fourth application dates as compared to the first. In discussing reasons for observed diurnal variations in vertical vapor flux of dieldrin and heptachlor applied to pasture, Taylor et al. (1977) concluded the phenomenon was directly related to diurnal variation in solar radiation input. The authors qualify this statement with the hypothesis that solar radiation is one factor that may be singled out as a source of vapor flux variation, as solar radiation input affects all other parameters of the complex relationship between the crop microclimate and the adjacent atmosphere. One parameter which solar radiation most definitely affects is the temperature at the leaf surface, which has a direct effect on the rate of volatilization. A similar conclusion was reached by Phillips (1974) from the results of laboratory experiments in which the volatilization rate of dieldrin from glass and cotton leaf

Figure III-3. Diurnal Azinphosmethyl Airborne Residues at Sampling Heights Between 0.5 and 6.0 Meters Above the Orchard, Measured at the Downwind Locations During the First Spray Period of the 1978 Season



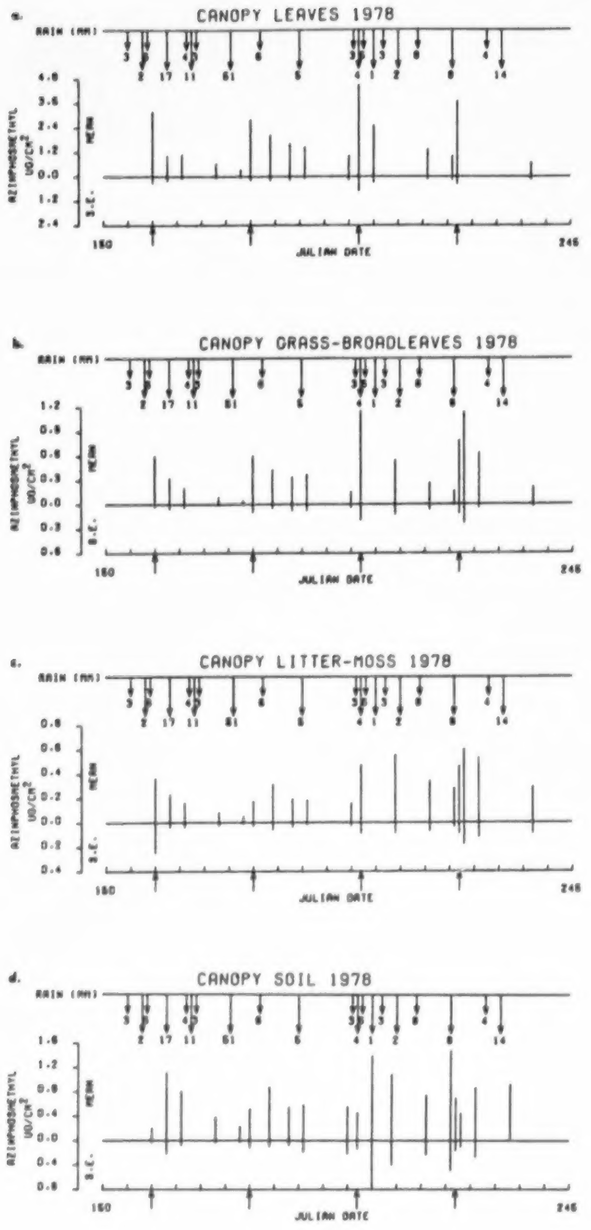


Figure III-4(a-d). Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1978 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.

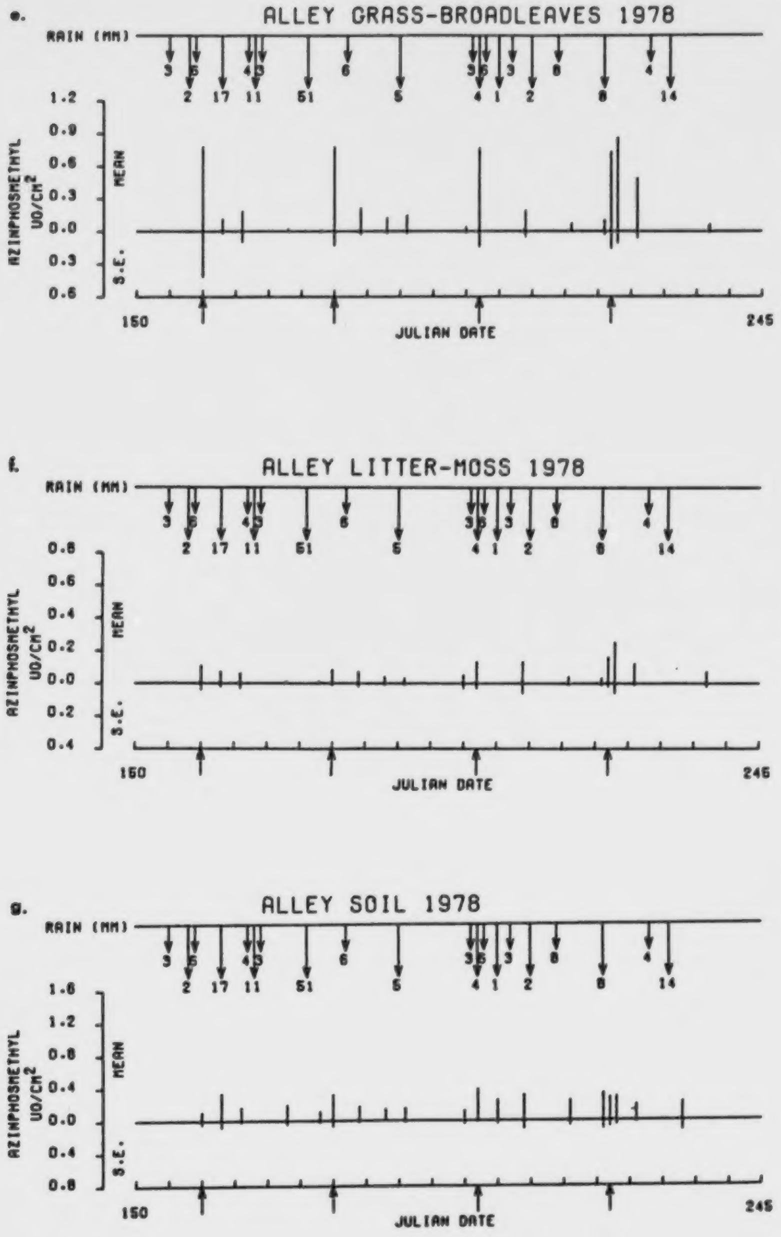


Figure III-4(e-g). Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1978 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.

surfaces was measured at various temperatures and wind speeds. Phillips stated that "clearly the factor having the most dramatic effect on loss was temperature." These observations would suggest that a possible partial explanation for differences in airborne concentrations measured in the afternoon on successive spray dates may be the differences in solar radiation input. The average solar radiation (cal/cm^2/min) measured during the afternoon sampling periods on each of the four application days was as follows: 1.11 on June 9, 1.06 on June 29, 0.57 on July 21, and 1.00 on August 10. The value of 1.11 cal/cm^2/min on June 9 was 100% of the available solar radiation (cloudless day). June 29 was also clear, July 21 was cloudy, and August 16 was partly cloudy. Comparison of solar radiation with the average airborne pesticide concentration measured at the center location (Location 6, Figure III-1) for these application days (Table III-1) shows a nonlinear trend with the highest airborne residues on June 9, which had the highest solar radiation input, and the lowest airborne residues on July 21, which had the lowest solar radiation input. In addition to solar radiation, the influence of wind speed on the airborne pesticide concentrations measured was also examined. In the comparison of the mean wind speed at 6.0 meters (see Table III-1) measured during the afternoon sampling period (1300-1500 hr) with the average airborne pesticide concentration measured at the center location for the four application dates (Table III-1), a nearly linear relationship was observed. Again the June 9 application date, on which the highest airborne pesticide concentrations were measured, also had the highest mean wind speed. The July 21 application date, on which the lowest airborne pesticide concentrations were measured, had the lowest mean wind speed (none detected, < 0.5 m/s). Phillips (1971) demonstrated using wind tunnel experiments that there was a marked increase in the rate of loss of dieldrin deposits on glass surfaces at wind speeds of 3.2 Km/hr (.89 m/s) as compared to still air. Dieldrin was deposited as a thin film in a manner designed to prevent mechanical loss from wind. We feel that increased wind speed is responsible for increased loss in azinphosmethyl deposits in the orchard. Both volatilization and wind erosion are mechanisms thought to be affected by wind speed. What is not clear is whether increased airborne loss of deposits due to increased wind speed should be reflected in the increased airborne pesticide concentrations measured, as increased wind speed, although removing more pesticide, would have a diluting effect on concentrations measured in the air. It is possible that wind erosion of freshly deposited residues is responsible for the marked difference between airborne residues measured the afternoon of June 9 and those measured the afternoon of July 21. The combined effect of wind speed and solar radiation input must also be considered. Further data collection under a variety of environmental conditions (actual and/or simulated) is needed to better describe the processes contributing to pesticide airborne loss.

On sampling dates following the application date, more often than not, airborne pesticide residue levels measured at 6.0 meters exceeded those measured at 0.5 or 1.0 meter. Six meters is twice the average tree height. One wonders how far above the orchard airborne residue levels are measurable. The data recorded did not allow estimation of horizontal airborne residue flux by direct methods. Estimation of either pesticide vertical airborne flux or mass horizontal flow of pesticide vapor by aerodynamic methods requires knowledge of wind speed profiles. Reliable interpretation of these profiles requires minimal fluctuation in atmospheric turbulence. While this criterion may be satisfied by uniform stands of short crops (Parmele et al., 1972; Taylor et al., 1977), the orchard profile does not satisfy it. An indirect estimate utilizing both deposit pesticide residues and airborne residues is presented as an alternative approach.

Hartley (1969) proposed that the volatilization rate (F_b) of one pesticide, from a non-adsorbing surface, could be predicted from that (F_a) of another pesticide, given the vapor pressures (P) and molecular weights (m) of the two compounds, by the following equation:

$$F_b = \frac{P_b(m_b)^{1/2}}{P_a(m_a)^{1/2}} F_a \qquad \text{(III-1)}$$

This relationship assumes that vapor flux is solely a function of molecular diffusion through the stagnant air closely surrounding the surface. Taylor (1978) points out that when examining vapor flux from plant surfaces, this equation is valid only during the time when there is complete coverage of the plant surface, i.e., when the pesticide vapor pressure is not reduced due to adsorption and is in effect volatilizing from itself. As the deposits become increasingly smaller the vapor flux is no longer strictly a function of molecular diffusion, but also a function of the degree of adsorption to the plant surface. In addition residue may penetrate leaf tissues or accumulate in cracks and fissures in the epicuticular wax superstructure or leaf specialized structures. With these limitations in mind, equation (III-1) was used to predict the airborne loss of azinphosmethyl from the orchard using dieldrin vapor flux over orchard grass determined by Taylor et al. (1977), along with vapor pressure data found in the literature. Using the aerodynamic model described by Parmele et al. (1972), Taylor et al. (1977) estimated the dieldrin vapor flux to be 80.4 g/ha/hr during the 1300 to 1500 hours sampling period 3.5 hours following application.

The vapor pressure reported dieldrin is 2.6×10^{-6} mm Hg at 20°C (Spencer and Claith, 1969). Only an upper limit for the vapor pressure of azinphosmethyl has been reported; $< 7.5 \times 10^{-6}$ mm Hg (no temperature given, Schrader, 1963). The vapor pressure of the ethoxy analog, azinphos-ethyl is given as 2.2×10^{-7} mm Hg at 20°C by Ouellette and King, 1977. To better estimate the vapor presuure of azinphosmethyl from the data available, the relationship between the possible crystal structures of these two analogs was examined. Rohrbaugh et al. (1976) examined, using xray diffraction crystallography, the crystal and molecular structure of azinphosmethyl. The unit cell stereograph depicted indicates that crystal structure is dictated, in part, by overlapping of the nearly planar ring systems and by intermolecular repulsion effects of the methoxy groups; the repulsion working against the packing forces of the crystal. The increased size of the ethoxy group of azinphosethyl should result in weaker packing forces by increasing the allowed distance between molecules. This effect is in turn reflected in the heat of sublimation, which varies directly with the magnitude of the packing forces, and the observed vapor pressure, which varies inversely with the magnitude of the heat of sublimation (Barrow, 1966). In addition, the melting point of azinphosmethyl (7374°C) is approximately 18° higher than azinphosethyl (56°C), indicating stronger packing forces and therefore a lower vapor pressure. Based on these observations, it was estimated that the vapor pressure of azinphosmethyl was slightly less than 2.2×10^{7} mm Hg at 20°C, the vapor pressure of its ethoxy analog. This value was used in equation (III-1) as P_b, along with dieldrin vapor pressure of 2.6×10^{-6} mm Hg at 20°C as P_a, and 80.4 g/ha/hr, the field durnal vapor flux (1300-1500 hr) as ${}_f a$, to give an upper limit estimate for azinphosmethyl diurnal airborne flux (1300-1500 hr) of 6.2 g/ha/hr. To examine the sensitivity of equation (III-1) to vapor pressure data, the value of 1.0×10^{-7} mm Hg, reported as the maximum for azinphosmethyl vapor pressure by Schrader (1963), was also used, resulting in an estimated azinphosmethyl diurnal airborne flux of 2.82 g/ha/hr. These predicted values of azinphosmethyl diurnal flux (1300-1500 hr) from the orchard are by no means precise estimates, but rather crude approximations, due in part to the general nature of the azinphosmethyl vapor pressure data. Other sources of variation are the differences in application rate (5.6 Kg/ha a.i. for dieldrin vs. .65 Kg/ha a.i. for azinphosmethyl), and the increased influence of wind that tree deposits may receive as compared to grass deposits. In theory, if there were complete coverage in both experiments the application rate should have little effect, as the vapor flux is independent of the amount of pesticide applied. As both pesticides were applied as water base sprays, which are deposited on plant surfaces as droplets, complete coverage is doubtful (Taylor, 1978). Under these "nonideal" conditions, vapor flux is no longer independent of the amount of pesticide present. As stated earlier, one explanation for the dependency of vapor flux on pesticide deposit residues is the hypothesis that incomplete coverage affects the apparent vapor pressure of the pesticide due to adsorptive effects of the foliar surface. Depending on the degree of coverage, part of the pesticide deposit will be unencumbered by external adsorptive effects and will evaporate at the maximum allowable rate (governed only by molecular diffusion through the stagnant layer); the remaining portion of the pesticide deposit will volatilize at some slower rate, depending on the degree of adsorption. To approximate the effect of foliar adsorption (i.e., incomplete coverage) on the vapor flux predicted in equation (III1), it was assumed that the higher the application rate the greater the percentage of the pesticide deposit that is affected by foliar adsorption. This is a necessarily simple approximation of a complex phenomenon, as additional factors including formulation, spray droplet size, climatic conditions during application, and characteristics of the foliar surface may influence the state of the pesticide deposit and the volatilization rate (Ebling, 1963; Hartley, 1969; Hull, 1970). With these limitations in mind, equation (III-1) was modified in the following manner

$$F_b = \frac{P_b(m_b)^{1/2}}{P_a(m_a)^{1/2}} \cdot F_a \cdot \frac{D_b}{D_a} \qquad \text{(III-2)}$$

where D_a is the application rate of pesticide a and D_b is the application rate of pesticide D_b. As 75% of the pesticide deposited in the orchard was applied to the trees, tree surface area must be considered when comparing airborne loss from the orchard with that of a grass field. Therefore the application rate of azinphosmethyl was based not only on the .263 ha of ground area but also the .276 ha of tree surface area. The average application rate for the first spray period of 1978 was 0.65 Kg/ha a.i. Three fourths was applied to .276 ha tree surface area and one fourth to .263 ground surface area. If the tree and ground surface areas are weighted by the proportion of the pesticide they receive and averaged, the adjusted application rate is 0.63 Kg/ha a.i. This value was divided by 5.6 Hg/ha a.i. of dieldrin applied to the grass pasture to give a D_b/D_a ratio in equation (III-2) of .112. In using this ratio as a crude approximation of foliar adsorptive effects on vapor flux, it must also be assumed that both application rates represent pesticide deposits that are less than or equal to complete coverage. The azinphosmethyl flux estimates determined from equation (III-2) were 0.697 g/ha/hr, using 2.2×10^{-7} mm Hg and 0.317 g/ha/hr using 1.0×10^{-7} mm Hg for the vapor pressure of azinphosmethyl. Diurnal airborne loss during this sample period, for the remaining dates samples, was estimated by assuming this loss is directly proportional to the measured horizontal flux ($g \cdot m^{-2} \cdot s^{-1}$) at 3.0 meters, determined from airborne pesticide concentrations (Table III-6) and wind speed measurements at 3.0 meters taken during sampling (Table III-1). Daily airborne loss was estimated on the work of Taylor et al. (1977), who reported as marked diurnal change in volatilization rates of dieldrin and heptachlor, when applied to orchard grass. Similar diurnal variations were reported by Taylor et al. (1976) for soil incorporated dieldrin. These researchers measured a peak flux early in the afternoon with virtually no volatilization measured before 0500 or after 2300 hr. Based on these findings, daily diurnal airborne loss was estimated assuming peak flux occurred during the two-hour sampling period between 1300 and 1500 hr, that no airborne loss occurred before 0500 or after 2300 hr, and that the loss rate varied linearly between the end points and the peak. Integration of the area under the triangle formed gives a daily airborne loss of 9.0 times the peak hourly flux measured between 1300 to 1500 hours. To estimate the loss occurring during the afternoon of the first day (from 1300 to 2300) one-half the daily estimate, or 4.5 times the peak flux, was used. Table III-7 shows the estimated daily airborne loss of azinphosmethyl from the orchard for the first spray period of the 1978 season. Loss is shown both as an absolute loss in g/ha and also as a percentage of the total dislodgeable residues and soil residues present on a given sample date. No daily loss estimate on a percentage basis was made for the application date as absolute loss shown is the estimated loss from 1300 to 2300 hr, rather than the entire day. These estimates suggest a marked decline in the daily airborne loss over the 18-day sample period. As a part of the parameterization of the model presented in Chapter II, first-order rate constants were determined for the disappearance of azinphosmethyl foliar dislodgeable residues and soil residues in each canopy and alley layer (accounting for movement). If these individual rate constants are weighted by the proportion of the total dislodgeable residues and soil residues which they attenuate, the average attenuation rate is 5.1%/day. The estimated air loss rate on day 3, based on measurements made at the downwind edge (Table III-7, Column 1), is 1.86%/day. This loss rate represents approximately 36% of the total attenuation. By day 6 air loss is 15%, day 13 it is 5%, and on day 18 air loss represents 8% of the total attenuation. These observations indicate that initially airborne loss plays a major role in the overall attenuation dislodgeable residues, however, this contribution crops off rapidly between 3 and 6 days following application. The change in the rate of airborne loss is believed to be a function of the state of residue deposits with the loosely bound residues being rapidly lost to the atmosphere soon after application. The remaining more tightly adsorbed and/or protected dislodgeable residue deposits volatilize at a slower rate. The effects of rainfall on the state of the pesticide deposits within the orchard must also be considered (see Chapter I). Certainly rainfall events that occurred during the first spray period (see Figure III-4) had an effect on the pesticide airborne concentrations and deposit residues measured. Again, loosely bound residues should be most susceptible to rainfall effects redistributing these residues to other parts of the orchard or as runoff leaving the orchard. These redistributed residues may no longer be loosely bound, as they may be more evenly distributed over a larger foliar surface than at application. By contrast,

TABLE III-7. ESTIMATED AZINPHOSMETHYL DAILY AIRBORNE LOSS FROM THE ORCHARD, FIRST SPRAY PERIOD OF THE 1978 SEASON

Days After Application	Mean Horizontal Flux at 3.0 m During Sampling (1300-1500) ($\mu g\ m^{-2}s^{-1}$)	Estimated Loss[a] During Sampling $g\ ha^{-1}\ hr^{-1}$		Estimated Daily Loss[b] $g\ ha^{-1}$	da^{-1}	96 day^{-1}	
		Downwind Edge					
0		1	2	1	2	1	2
3	10.6	.697	.317	.313[c]	1.43[c]		
6	2.4	.158	.072	1.43	0.65	0.4	0.34
13	0.4	.026	.012	0.24	0.11	0.24	0.11
18	0.4	.026	.012	0.24	0.11	0.43	0.20
		Center					
0	11.5	.697	.317	3.13[c]	1.43[c]		
3	5.7	.345	.157	3.11	1.41	1.51	0.68
6	1.2	.073	0.33	0.65	0.30	0.34	0.16
13	0.5	.030	.014	0.27	0.12	0.27	0.12
18	0.4	.024	.011	0.10	0.10	0.39	0.18

---

[a] Based on the estimated airborne loss at peak flux (1300-1500 hr) on day 0, calculated using 2.2×10^{-7} mm Hg at 20°C (column 1 and 1.0×10^{-7} mm Hg (column 2) for the V.P. of azinphosmethyl in equation (2). Diurnal loss for the remaining sample dates was estimated by assuming this loss is directly proportional to the measured horizontal flux at 3m.

[b] Daily diurnal loss was estimated assuming peak flux during the 2 hr sampling period (1300-1500 hr), that no airborne loss occurred before 0500 and after 2300, and that the loss rate varied linearly between the end points and the peak. The daily loss in % da^{-1} was determined by dividing the daily loss in grams by the total $g\ ha^{-1}$ dislodgeable residues (including soil residues) remaining.

[c] One-half day estimate.

residues that were initially distributed to protected plant areas could be redistributed with rainfall so as to increase their susceptibility to airborne loss. Rainfall may also enhance volatilization; if the soil moisture level is low prior to a rainfall event, the increased soil water may displace adsorbed pesticide, increasing its effective vapor pressure at the soil surface (Spencer et al., 1973). Heavy rains on unsaturated soils may also move initially displaced pesticide to lower soil depths (Spencer and Claith, 1977; Helling et al., 1971).

In the model described in Chapter II, movement is separated from overall attenuation only, and this attenuation process is assumed to be first order. Modeling pesticide disappearance using first-order kinetics assumed that the individual attenuation processes are first order and strictly additive, giving an exponential decay of pesticide residues with time. As early as 1955, Gunther and Blinn proposed that the first-order loss curve was an approximation of a bilinear or trilinear loss curve. This hypothesis was again proposed by Gunther et al. (1969, 1977), by Hill (1971), and Van Dyk (1974, 1976). Taylor et al. (1977) indicated that the disappearance of heptachlor and dieldrin from orchard grass and soil could be attributed solely to airborne loss. They represented pesticide loss as a bilinear process with two regression equations; one for days 1 to 5 and another for days 5 to 107. Stamper et al. (1979) proposed an alternative to first-order kinetics for foliar applied insecticides, showing for a number of foliar applied organophosphate insecticides, that ln concentration versus ln time gave a linear relationship with a better correlation coefficient than the linear relationship established by plotting ln concentration versus time (which indicates first-order kinetics). The author suggests the reason the ln-ln plots give a better linear relationship is that one form of the equation describing the fitted line is in agreement with equations describing molecular diffusion from small volumes. Their solution is interesting, but the use of ln time would not be compatible with the algorithms used in the model presented in Chapter II.

A third approach to modeling airborne loss was proposed by Phillips (1971). He suggested that a double exponential equation

$$T = A_e^{-kt} + B_e^{-k't} \qquad \text{(III-3)}$$

may apply when two volatilization processes are occurring simultaneously at different rates. This model was later proposed by Popendorf and Leffingwell (1978) to explain the observed bilinear loss of parathion dislodgeable residues on citrus foliage. The approach used here is an extension of the double exponential equation. At the present, residues deposited in the orchard are classified as either dislodgeable, surface-penetrated, or soil. This classification is based on analytical procedures for the recovery of these residues as outlined in the experimental section. Dislodgeable residues are pictured as residing on the foliar surface, whereas surface-penetrated residues are embedded on or in the cuticular matrix. Further penetration, resulting in tissue bound residues, is also thought to occur (Wieneke and Steffens, 1974). To model airborne loss, it was assumed that a portion of the dislodgeable residues are loosely bound. The loss of these residues to the atmosphere therefore being only slightly affected by the adsorptive effects of the leaf surfaces. The remaining dislodgeable residues are more tightly bound and volatilize more slowly. A similar theory for the decrease in the daily airborne loss rate of foliar applied pesticides is presented by Taylor (1978). Volatilization of surface-penetrated and tissue-bound residues is thought to be neglible and the kinetics of the disappearance of these residues is not treated here. Making these assumptions, pesticide airborne loss from foliar surfaces is represented in the differential form as:

$$\frac{dT}{dt} = -a_1D(t)-a_2L(t)-a_3T(t) \qquad \text{(III-4)}$$

where t is time in days, D is dislodgeable residues, L is loosely bound residues, T is total residues (dislodgeable plus loosely bound residues, and excluding penentrated residues), a_1 is the air loss rate of the tightly bound dislodgeable residues, a_2 is the air loss rate of loosely bound residues, and a_3 is the attenuation rate of the total residues (other than air loss and assumed to be independent of binding state). The constant a_3 is thought to be primarily a function of degradation at the foliar surface and penetration to subsurface tissues. As T = D + L, equation (III-4) can be reduced to:

$$\frac{dT}{dt} = -(a_1 + a_3)D(t)-(a_2 + a_3)L(t) \qquad \text{(III-5)}$$

and therefore:

$$\frac{dD}{dt} = -(a_1 + a_3)D(t) \qquad \text{(III-6)}$$

and

$$\frac{DL}{dt} = -(a_2 + a_3)L(t) \qquad \text{(III-7)}$$

As loosely bound residues are what their name implies, these residues are more easily lost to wind erosion and volatilize at a rate governed only by diffusion across the stagnant air layer. Consequently it is assumed that airborne loss of these residues is responsible for the observed early rapid decay of total residues; this loss is represented by Gunther et al. (1958) and more recently by Popendorf and Leffingwell (1978) as the first phase of a bilinear loss pattern. With the disappearance of these residues from the foliar surface the rate of decline of remaining dislodgeable residues is primarily responsible for the observed rate. The loss rate of these more tightly bound residues is determined by the combination of airborne loss (a_1), degradation and penetration (a_3) of the remaining dislodgeable residues. This represents the second phase of an observed bilinear loss pattern. As current sampling or analytical techniques cannot distingusih between loosely bound and more tightly adhered dislodgeable residues, D, L and the rate constants a_1, a_2 and a_3 were determined indirectly. In determining the two rate constants in the double exponential equation, Popendorf and Leffingwell (1978) used dislodgeable residue data and a constrained optimization procedure that compared predicted and observed values. As the hypothesized mechanism for the observed bilinear loss of foliar applied pesticides presented here is based on the assumption that early pesticide disappearance is primarily due to airborne loss, the change in the estimated daily airborne loss rate was used to estimate when the loosely bound residue deposits approached zero. If the daily air loss rates (average of center and downwind edge estimated in Table III-7, Column 1) are examined, it is noted that there is a sharp decrease in the rates between day 3 (1.69%) and day 6 (0.54%). The average rate and standard deviation for days 6, 13, and 18 is 0.40% ± 0.18%. It was therefore assumed that the loosely bound residues disappeared between 3 and 6 days following application and that the average daily air loss rate of 0.40% represented the air loss rate (a_1) of tightly bound dislodgeable residues. The total loss rate ($a_1 + a_3$) of the tightly bound disdodgeable residues was determined from a least squares linear regression of log g/ha total residues versus time since applications, for days 3, 6, and 13 of the first spray period. Total residues included foliar dislodgeable residues and soil residues. Soil was included to give a conservative estimate with respect to movement of residues present in the orchard following rainfall events. Day 18 was omitted from this analysis as it was felt that the 51.3 mm (2.1") of rainfall the orchard received on day 16 redistributed the residues in such a manner as to not allow a conservative estimate of residues present. From this analysis the daily loss rate ($a_1 + a_3$) was determined to be 7.5% (r^2 = .958). This rate is considerably faster than the daily attenuation rate of 4.2% (r^2 = .985), determined from total residues for days four to 20 of the second spray period of the 1978 season. Only one rainfall event occurred during the second spray period (5.1 mm on day 10), whereas 17.3 mm of rainfall fell just prior to day 3, and 16.8 mm fell between days 3 and 13 of the first spray period (see Table III-1 and Figure III-2). This would suggest that the disappearance of these residues was influenced by rainfall (although other environmental parameters such as wind speed, solar radiation, humidity, or some combination of the above also may have contributed). The results may have been that the pesticide residues measured during the first spray period were not conservative (i.e., movement of pesticide to unsampled soil depths, pesticide carry-in with moisture uptake by litter and foliar surfaces, increasing the penetrated residue pool). Also, as stated earlier, rainfall may have redistributed foliar residues as to allow increased volatilization. An influx of moisture at the soil surface may have also caused an increase in volatilization. That this may be the case is suggested by the increase in the estimated average daily air loss rate between day 13 (0.26%) and day 18 (0.41%) (Table III-7, Column 1). Until the effects of rainfall and other climatic conditions on pesticide disappearance can be adequately differentiated, of the daily attenuation rate ($a_1 + a_3$) to this set of environmental conditions must be assumed. Given a_1 to 0.40% and $a_1 + a_3$ to be 7.5%, then a_3 is 7.1%. L and a_2, the amount and rate of airborne loss of the loosely bound residues, were estimated using an optimization routine similar to that employed by Popendorf and Leffingwell (1978). Equation (III-3) was rearranged to solve for T (total residues) at some sample date L:

$$T(k_i) = D(k_{i-1}) \quad (1-(a_1 + a_3))^{(k_i - k_{i-1})} + L(k_{i-1}) \quad (1-(a_2 + a_3))^{(k_i - k_{i-1})} \qquad \text{(III-8)}$$

At T is known at sample dates k_i = 0,3,6,13, and a_1 and a_3 have previously been estimated, values for L and a_2 were tried in equation III-8 to give a minimum value for the test statistic:

$$\frac{T_i - (L_i + D_i)^2}{T_i} \qquad \text{(III-9)}$$

Using this statistic, it was estimated that 37.5% of azinphosmethyl dislodgeable residues, initially deposited in the orchard, were loosely bound. The daily air loss rate (a_2) of the loosely bound fraction was estimated to be 90% day^{-1}. This indicates a rapid loss of approximately one third of the residues to the atmosphere, resulting in the disappearance of this fraction in approximately 3 days. It is also suggested that loss of the remaining dislodgeable residues is governed by a much slower air loss rate and attenuation at the foliar surface. Figure III-5 shows the solution to equation (III-5) as a line through the observed residue values (total dislodgeable residues and soil residues) for the first spray period of the 1978 season.

The proportion of azinphosmethyl deposit residues estimated to be loosely bound and the rate of loss of this fraction is thought to be a function of factors associated with application, environmental conditions, and orchard characteristics. This is suggested by the difference in the decline of total dislodgeable and soil residues between the first and second spray periods as shown in Figures III-5 and III-6. Parameterization of equation (III-4) using the residue data from the second spray resulted in an estimate of 7.7% for the loosely bound fraction (L) with an estimated daily air loss rate (a_2) of 30% day^{-1} for this fraction. The rate constant $a_1 + a_3$ was determined from linear regresssion of the total dislodgeable and soil residues for days 4 to 20 to be 4.2% day^{-1} (r^2 = .985). The air loss rate (a_2) of the dislodgeable fraction (D) was assumed to be the same as determined for the first spray periods, 0.4% day^{-1}. The lack of an initial period of rapid loss during the second spray period may have been due solely to the lesser amount of rainfall received, as compared to the first spray period. That rainfall may affect airborne loss has been discussed earlier. In addition, rewetting of the residue deposit may enhance penetration and plant uptake (Hull, 1970; Bukovac, 1976), resulting in an increase in the observed loss rate of dislodgeable residues. The effects of other environmental parameters (i.e., solar radiation, ambient temperature, relative humidity, wind speed and atmospheric stability) should also be considered.

To better understand the influence of those factors associated with the formulated pesticide, its application, and environmental conditions on the attenuation of residue deposits in orchards, a more thorough sampling program of both airborne and deposit residue is required. The pesticide should be applied and its disappearance monitored under a variety of properly characterized "natural conditions." The multi-component kinetic model presented here provides a tool for investigating those parameters that influence pesticide airborne loss and the overall attenuation of deposit residues.

Figure III-6. Decline in Total Azinphosmethyl Dislodgeable and Soil Residues Measured During the Second Spray Period of the 1978 Season

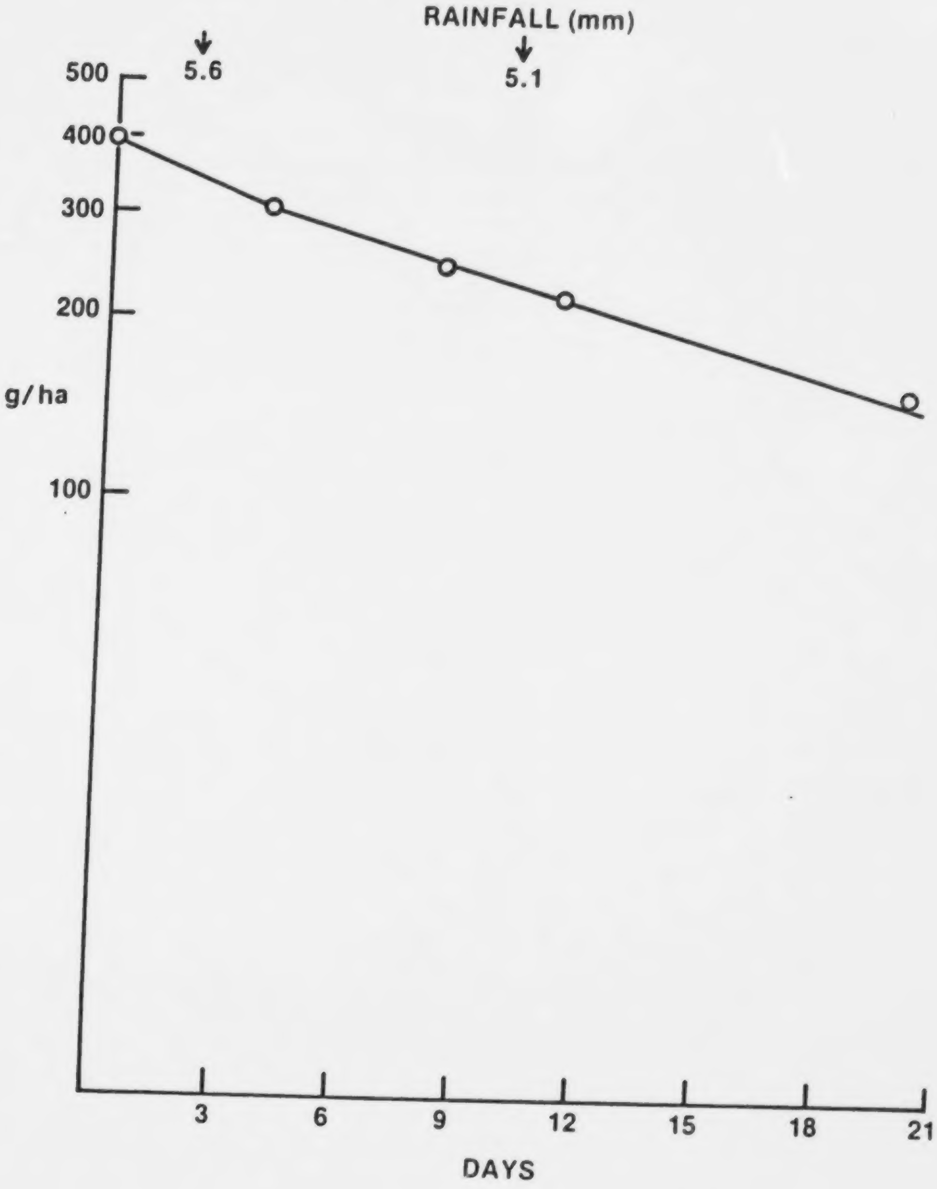
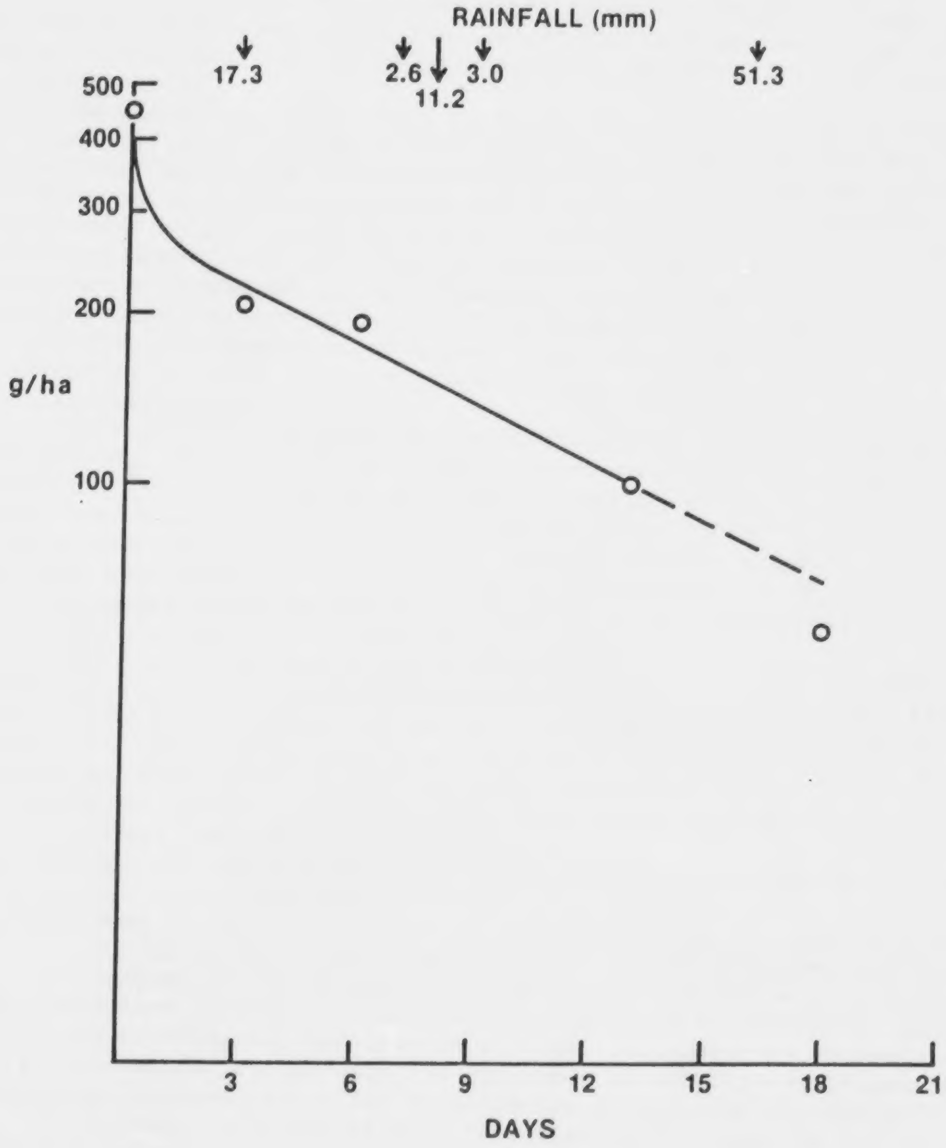


Figure III-5. Decline in Total Azinphosmethyl Dislodgeable and Soil Residues Measured During the First Spray Period of the 1978 Season



CHAPTER IV

GENERALIZATION OF THE PESTICIDE FATE MODEL

INTRODUCTION

It would be unrealistic to believe that a model of pesticide fate in any terrestrial ecosystem, driven by time and rainfall conditions only, would be capable of explaining all the variation observed in the field data. To better explain the variation observed, both movement and attenuation should be decomposed to represent their component physical, chemical, and biological processes, each a function of the relevant environmental parameters (i.e., solar radiation, temperature, humidity, wind speed, atmospheric stability, etc.).

The conceptual model shown in Figure II-1 of Chapter II was developed to represent those processes which determine the distribution and fate of a pesticide applied to an orchard ecosystem. The initial mathematical form of the model describes azinphosmethyl fate in terms of attenuation and movement, based only on field data from three seasons. The attenuation rate constants determined represent the combined effects of a number of individual processes as indicated in the conceptual model. These processes are individually influenced by different combinations of environmental parameters. In addition, because these processes occur simultaneously, the use of field experiments to study their individual contribution to the overall attenuation rate is difficult.

Laboratory experiments, designed to isolate and study individual processes under controlled environmental conditions, are at present the preferred method for studying environmental fate. Such experiments, while giving the researcher much greater control of the variables involved, often do not give results that can be extrapolated to the real world. However, much progress has been made recently in determining rate constants for a number of attenuation processes under various sets of environmental conditions (Zepp et al., 1975; Smith et al., 1977; Freed et al., 1979).

Laboratory experiments should be designed to isolate and examine the influence of selected environmental parameters on the individual processes that in combination result in the observed field attenuation and movement rates. In addition, in situ field rate data should be collected under a variety of "natural conditons" to allow the partial isolation of individual environmental effects. Further model development and experimental design should address the following questions:

(1) How are various processes influenced by individual environmental parameters and compound properties, and
(2) What is the contribution of each process to the overall attenuation and/or movement rates under a given set of environmental conditions.

The purpose of the present study was to refine and develop further the model described in Chapter II, using in situ field measurements, data from laboratory experiments, and results of other laboratory experiments reported in the literature, to describe the influence of selected environmental parameters and compound properties on pesticide attenuation and movement.

The mathematical form used to represent each process in the model is described below, together with its default parameters for azinphosmethyl in our experimental orchard. The user can alter these values to describe other compounds or situations. The present model can be greatly improved in both form and parameter values as the results of future field and laboratory studies become available.

The Attenuation Submodel

In Chapter II a matrix A of daily attenuation rates of azinphosmethyl in various orchard layers was developed. The orchard is treated as four vertical layers (tree, grass-broadleaves, litter-moss, and soil) by two horizontal areas (canopy, alley). Seven regions (no alley tree region exists) appear in each of the matrices and vectors below, beginning with canopy trees and proceeding to alley soil. Each diagonal element A_{ii} represents the fraction of azinphosmethyl lost from region i in one day, excluding any movement to or from another region (which is accounted for in matrices P, L, and H, the nonrain movement, light rain movement, and heavy rain movement matrices, respectively).

To investigate the influence of rainfall and other environmental parameters of pesticide loss, the attenuation matrix A may be decomposed into the diagonal matrices:

$$A = A_p + A_c + A_v + A_m + A_u$$

where the summand matrices A_p, A_c, A_v, A_m, and A_u represent photolysis, chemical degradation, volatilization, microbial degradation, and plant uptake, respectively, and are called the attenuation component matrices. Each of these matrices is a 7 x 7 diagonal matrix with one non-zero entry for each region. Each attenuation component matrix is decomposable into a diagonal matrix of constants (the rates under "standard conditions") and a set of functions which modify those rates based on environmental conditions. The "standard" rates for each process should sum to the field-determined values. To examine the feasibility of this approach to further model development, the relationship between azinphosmethyl degradation kinetics and a number of environmental parameters was determined from laboratory data and the results of other laboratory experiments reported in the literature. The volatilization kinetics of azinphosmethyl were discussed in Chapter III.

Pesticide degradative mechanisms have been reviewed by a number of researchers (Ebling, 1963; Crosby, 1973; Leonard et al., 1976). Pesticide degradation has been traditionally divided into three major areas: Chemical, photochemical, and biological. Pesticides may undergo a number of chemical transformations in the environment to include: hydrolysis and other nucleophilic reactions, oxidation, isomerization, reduction and free radical reactions (Goring et al., 1975). For the organophosphates, including azinphosmethyl, hydrolysis and oxidation are thought to be the most commonly occurring. Biological degradation is a major pathway for the disappearance of many pesticides in the soil (Kearny and Helling, 1969). The diverse microbial populations of most soils are capable of degrading pesticides with little difficulty, either by adaption, or more commonly, by co-metabolism (Matsumura, 1975). Microbial degradation on plant surfaces must not be excluded in assessing possible causes of pesticide disappearance (Steffens and Wieneke, 1975). Photochemical degradation of pesticides has been demonstrated in water and air and on soil and foliar surfaces (Crosby, 1969; Nilles and Zabik, 1975; Liang and Lichtenstein, 1976; Zepp and Cline, 1977).

Chemical Degradation

As with the overall attenuation rate, the rates for the individual processes are assumed to be first-order or pseudo first-order. Chemical degradation of azinphosmethyl is assumed to occur primarily by hydrolysis, but oxidation is also possible (Eto, 1974). Oxidation may occur in all regions. The oxidation rate is represented by

$$\frac{DC}{Dt}\,(\text{oxidation}) =_{\text{def}} R_{ox} = K_{ox}C$$

The most likely oxidation pathway is through the reaction with free radicals, assuming an excess of free radicals available for interaction ($r\cdot$generation $> K_{ox}$) then K_{ox} is rate limiting and the reaction is pseudo first-order (Smith et al., 1977). Photooxidation, as a result of reaction with photochemically formed free radicals, the oxygen triplet diradical, or the more reactive singlet oxygen, may be more responsible for many pesticide non-biological oxidations (Crosby, 1973; Khan, 1976). Soil free radicals may also be important in the oxidation of pesticides in this medium (Plimmer et al., 1967; Armstrong and Konrad, 1974). Spear et al. (1978) indicated that paraoxon production may be related to both ozone and dust levels on citrus in central California. Spencer et al. (1975) also noted paraoxon formation on dust and dry soil beneath citrus trees in southern California citrus foliage has also been indicated (Gunther et al., 1977). However, azinphosmethyl-oxon levels never exceeded 1.0% of the azinphosmethyl present. The oxon formed was more stable, but dissipated rapidly following rainfall. The likelihood that oxidation would contribute significantly to the degradation of azinphosmethyl during the relatively wet and humid summer months normally experienced in the temperate eastern United States is doubtful.

Hydrolysis has been shown to be an important mechanism of organophosphate degradation in both soil and aqueous environments (Freed et al., 1979). Hydrolysis resulting from reaction with moisture on foliar surfaces must also be considered. A discussion of hydrolytic mechanisms for the organophosphates in water can be found in Faust and Gomaa (1972) and Smith et al. (1977). The reaction is a function of pH, and can be either neutral, acid, or base-catalyzed. Again, the reacting species (H_2O, H^+, OH^-) were assumed to be in excess of the pesticide, and the reaction first order, at a given pH.

Azinphosmethyl aqueous hydrolysis as a function of pH was determined by the procedure of Freed et al. (1979). Buffers used were as follows: pH 1.0, 0.0 m KCl and 0.01 m HCl; pH 3.0 and 5.0, 0.01 m potassium hydrogen phthalate and 0.01 m NaOH; pH 7.0, 7.5, 8.0, 8.5, 9.0, 0.01 m TRIS and 0.01 m HCl. Azinphosmethyl concentration was determined by analysis of residual parent compound by GLC (see Chapter I). First-order rate constants at 25°C were determined from linear regression of log concentrations versus time, over a 20-day incubation period. Hydrolysis rate constants at pH 1, 3, 5, and 7 averaged 0.8% day^{-1} (standard deviation, 0.1%). The observed stability under neutral and acid conditions is in agreement with the observations of Liang and Lichtenstein (1972). Faust and Gomaa (1972) report that many organophosphates are stable under acid conditions. (Azinphosmethyl hydrolysis as a function of pH is shown in Figure IV-1). The relationship between pH and the base-catalyzed reaction rate (pH 7.5-9.0) is represented by the linear regression equation:

$$K_h = 0.095\ \text{pH} - .713\ (r^2 = .996) \qquad \text{(IV-1)}$$

where K_h is the aqueous hydrolysis rate constant (time^{-1}).

The rate of hydrolysis as a function of temperature was represented using the Arrhenius equation:

$$K_h = Ae^{-Ea/RT} \qquad \text{(IV-2)}$$

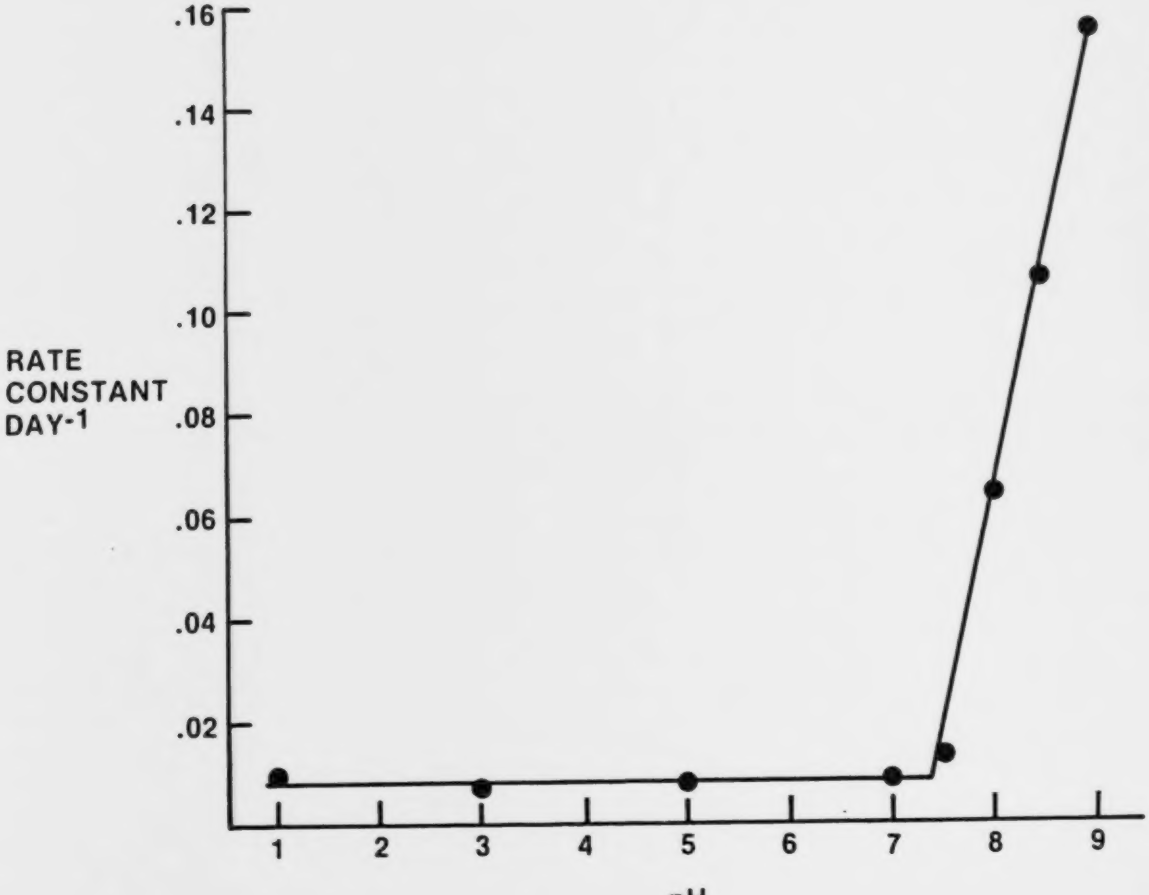


Figure IV-1. Azinphosmethyl Hydrolysis Rate Constant Versus pH

where K_h is the aqueous hydrolysis rate constant ($time^{-1}$) at temperature T, A is a constant depending on the chemical and other non-thermal factors, R is the gas constant, and Ea is the energy of activation. If K_h is determined over some temperature range, Ea can be calculated from the slope of the line, for a plot of log K_h versus 1/T. To estimate temperature effects on azinphosmethyl hydrolysis the data of Liang and Lichtenstein (1972) was analyzed using equation IV-2 as shown in Figure IV-2. The value determined for Ea, over the temperature range 5-50°C, was 12.5 Kcal/mole. This is an approximate value and will vary with pH and the temperature range used. Buffer composition and strength may also influence hydrolysis rates and associated values for Ea (Smith et al., 1977).

Hydrolysis of azinphosmethyl is assumed to be important in all regions. Although little is known about reactions occurring on foliar surfaces, it is assumed that, due to transpiration, there is an environment with sufficient moisture to allow hydrolysis to occur (Wieneke and Steffens, 1974). A neutral pH is assumed in all but the soil regions. Hydrolysis is treated as a function of air temperature only. This again is an approximation as temperature. In the soil regions hydrolysis is treated as a function of both soil temperature and pH. Properties of the soil which influence hydrolysis are discussed by Freed et al. (1979). Adsorption to clay and organic matter is thought to play an important role in degradation, as adsorbed organophosphates may be protected from hydrolysis or, in some cases, may result in increased reaction rates due to surface catalysis (Crosby, 1970). The use of the Arrhenius equation (IV-2) to represent the effects of temperature on hydrolysis and other non-biological degradative mechanisms in the soil environment is discussed in Hamaker (1972). This author suggests that the heterogenous nature of soils as a reaction medium may not allow the use of equation (IV-2) as it has traditionally been applied to reactions in homogenous solutions. This is indicated by the fact that the distribution coefficient, Kd (pesticide adsorbed/pesticide in solution), may change as the pesticide is transformed, and also by the exothermic nature of the adsorption process resulting in an equilibrium shift towards sorption to organic matter with increasing temperature (Felsot and Dahm, 1979). Because both these phenomena will influence the concentration of pesticide in the soil solution and, theoretically, the rate of hydrolysis, this suggests that the "A" term in equation (IV-2) is not a constant, but a function of both pesticide concentration and soil temperature. Until the influence of soil properties on hydrolysis is better understood, and for the purposes of this study, "A" is assumed to be constant. The data of Yaron et al. (1974) were used to determine the relationship between temperature and the azinphosmethyl hydrolysis rate constant in soil. Degradation rates for wet soil (50% of saturation) incubated at 6, 25, and 40°C, were used to parameterize equation (IV-2) as shown in Figure IV-3. The Ea determined from this data was 13.5 Kcal/mole. The soil used in this study was a silty loam, pH 8.4 and <1% organic matter. Both pH and soil type should be considered when comparing rates determined from the data in this particular study with other research. Soil in the orchard used in the present study was a marlette sandy clay loam, pH 6.0, 56% sand, 20% silt, 24% clay, and 6.0% organic matter in the top 10 cm. The results of degradation studies in the laboratory, using soil from the orchard (moisture content 30% = 48% of saturation) sterilized with sodium azide, fortified with 10 ppm azinphosmethyl, and incubated at 25 ± 1°C for 20 days, showed no degradation. This is not surprising considering the acid pH and the clay and organic matter content of the soil.

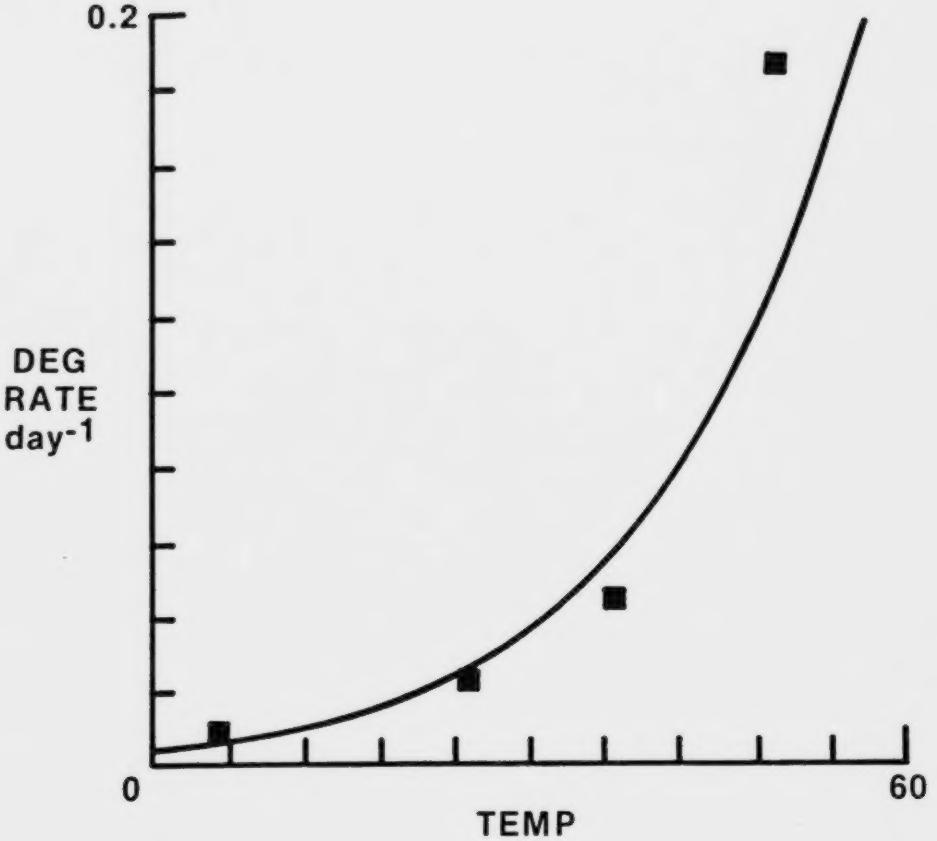


Figure IV-2. Azinphosmethyl Hydrolysis Rate Constant Versus Air Temperature

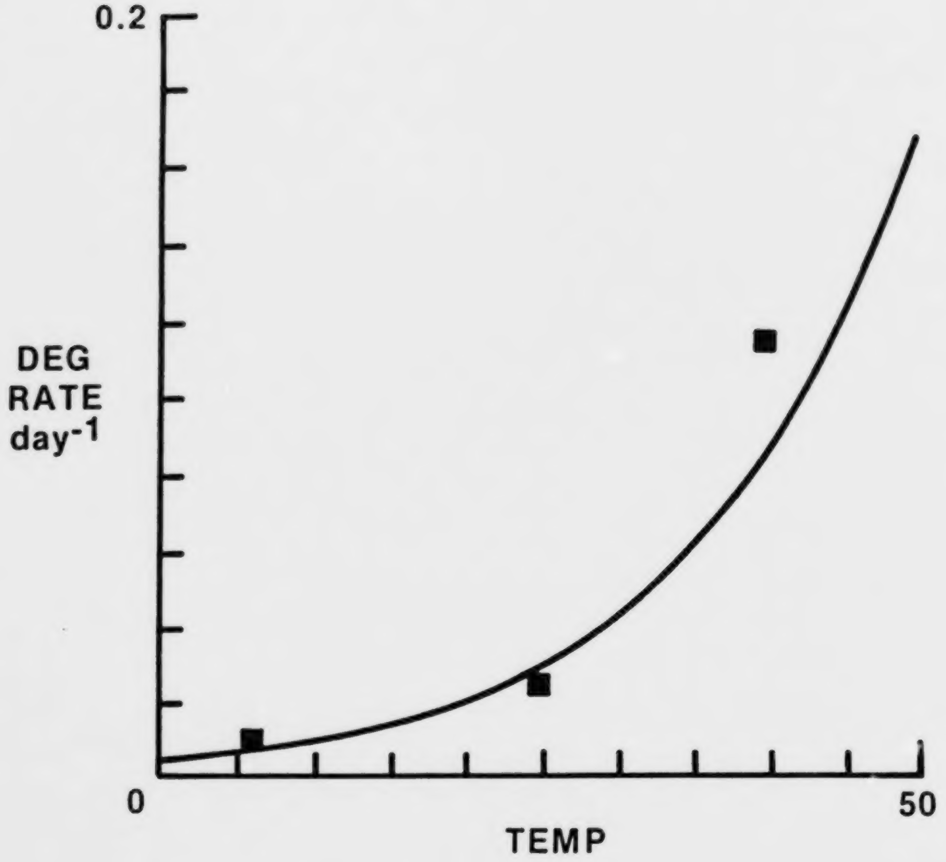


Figure IV-3. Azinphosmethyl Hydrolysis Rate Constant Versus Soil Temperature

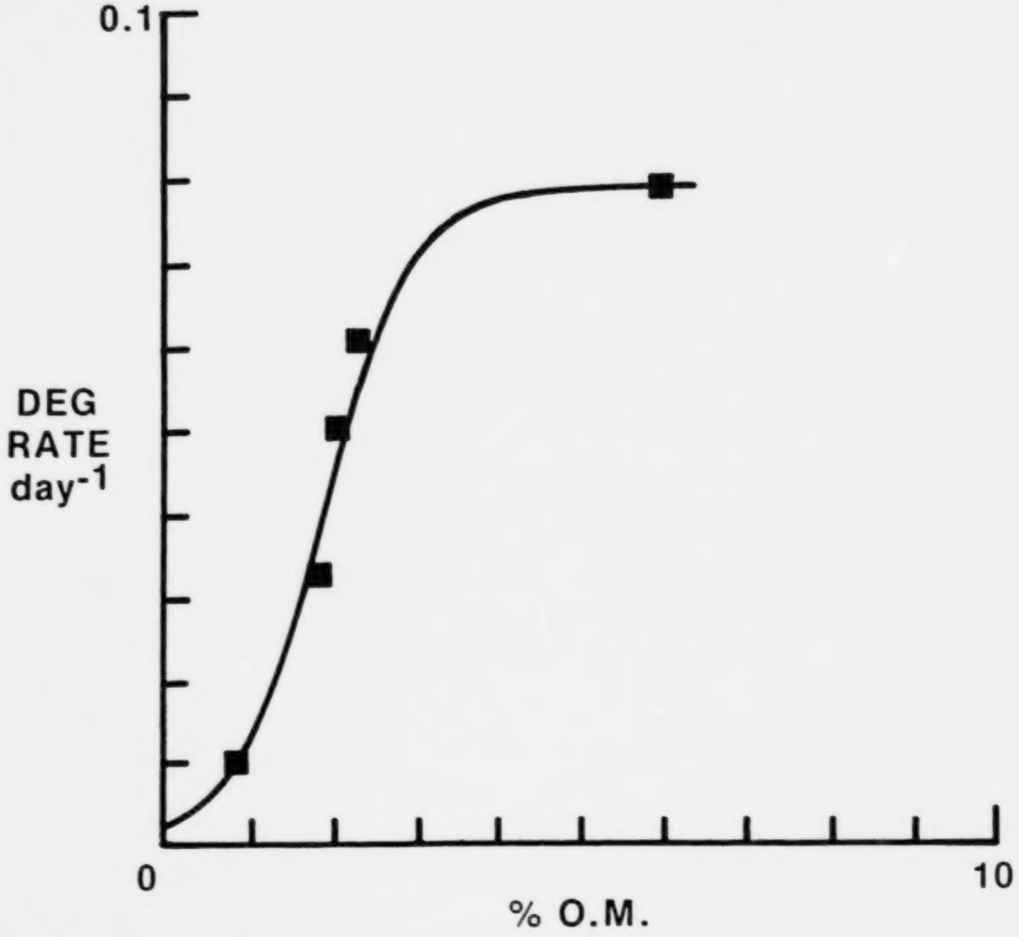


Figure IV-4. Azinphosmethyl Microbial Degradation Versus Soil Percent Organic Matter

Microbial Degradation

Although microbial degradation cannot be ruled out as contributing to the overall attenuation of residues deposited on foliar surfaces, microbial degradation is thought to be a major degradative pathway in the litter-moss and soil layers. In some instances, pesticides can be used as the sole food source of microorganisms, but more often they are co-metabolized with other organics. If the pesticide is used as a primary nutrient by the microorganisms of the soil, then a lag period may be observed following application while the soil microorganisms population adapts to the new food source. This period may become shorter with successive applications (Hamaker, 1972). With co-metabolism, no lag period should occur. This is the situation assumed to be present in the orchard soil and litter, with regard to azinphosmethyl biodegradation. The rate of biological degradation will therefore vary with the total available food source (i.e., organic matter content of the soil), temperature, and a moisture (Hamaker, 1972). To determine the microbial degradation rate, a 20-day incubation at 25 ± 1°C, of the non-sterilized orchard soil (moisture content 30% = 48% of saturation) fortified with 10 ppm azinphosmethyl, was performed. The first-order rate constant, determined from linear regression of concentration of azinphosmethyl remaining versus time, was 7.9% day^{-1} (r^2 = .969).

The influence of organic matter content of the soil on microbial degradation of azinphosmethyl was based on the data of Iwata et al. (1975). Soils in this study were passed through a 100 mesh sieve and moisture was added to 40% saturation. The soils were fortified at 450 ppm azinphosmethyl and incubated at 30°C. Characteristics of these soils and the corresponding azinphosmethyl degradation rates over a 20-day period are as follows.

TABLE IV-1. Azinphosmethyl Degradation when Incubated with Various Soils[a].

Soil	% Organic Matter	Mechanical Analysis, %			pH	K_m[b]	r^2
		Sand	Silt	Clay			
1	0.8	53.6	31.0	15.4	6.9	-.010	.992
2	1.8	56.0	33.0	11.0	7.6	-.033	.996
3	2.1	12.5	50.7	36.8	7.3	-.050	.991
4	2.3	22.4	34.5	43.1	7.3	-.061	.969
5	6.0[a]	56.0	20.0	24.0	6.0	-.079	.969

[a] Data for soils 1-4 reported in Iwata et al. (1975).
Soil was taken from the orchard used in the present study.

[b] Proportional daily loss determined from the data of Iwata et al. (1975) (Soils 1-4) and the orchard soil used in the present study (soil 5).

Figure IV-4 shows a plot of percent organic matter versus the azinphosmethyl degradation rate. Degradation is assumed to be primarily microbial, due to the neutral or acidic pH values for these soils. However, hydrolysis and other forms of chemical degradation may also have contributed to the observed rates derived from the data of Iwata et al. (1975). A modified form of the Verhulst-Pearl logistic equation (Pielou, 1969) was fit to the data to give the following relationship:

$$K_m = .079\ [1 + e^{-1.85(\%\ \text{o.m.}\ -\ 1.87)}]^{-1} \qquad \text{(IV-3)}$$

The correlation of azinphosmethyl degradation with a single soil factor (organic matter) must be interpreted with some caution, as the organic matter content may be correlated to other soil conditions effecting degradation. High organic matter is usually accompanied by a low soil pH, and adsorption has been shown to be positively related to organic matter content (Saltzman et al., 1972). Even though the data present here shows a positive correlation of degradation rate to organic matter content, a number of researchers have found that at very high organic matter contents of peat and muck soils, degradation is decreased, presumably due to adsorption (Beynon et al., 1966; Hamaker, 1972; Kaufman, 1964). In addition, the relationship between the data of Iwata et al. (1975) and that of the present study must be viewed in light of the differences in initial concentrations used. Hamaker (1972) cites a number of studies which indicate that the degradation rate, on a percentage basis, increases with decreasing concentration. The azinphosmethyl microbial degradation rate of 7.9% day^{-1} determined using an initial concentration 10 ppm, may have been lower if the initial concentration of 450 ppm, employed by Iwata et al., (1975) was used. Temperature differences between the two studies are not thought to be significant, as indicated by the temperature relationship shown in Figure IV-5.

The relationship between temperature and soil microbial degradation was determined from the data of Yaron et al. (1974). The difference in degradation rates between sterile and non-sterile wet soil (50% of saturation, incubated at 6°, 25°, and 40°C, was used to determine this relationship. The data was fit to the following polynomial equation:

$$K_m(t) = .00298T - .00005T^2 - .013 \qquad \text{(IV-4)}$$

where K_m is the microbial degradation rate at a given temperature, T. This fit shows the optimum temperature to be approximately 30°C. This is in agreement with the data of Day et al. (1961) for degradation of amitrole in soil. This temperature relationship is thought to reflect a response to temperature by the microorganism population. Changes in population size distribution, or adaption to degradation of the chemical may all be responsible for the observed temperature effect. The response may also be due in part to an Arrhenius type mechanism. At temperatures above the optimum (30°C) the rate no longer shows a positive relationship to temperature, possibly due to the heat lability of the microorganisms.

Soil moisture has also been shown to be an important factor in soil degradation of pesticides. The data assembled by Hamaker (1972) show much slower rates in dry as compared to moist soils and that rates tend to level off at higher moisture levels (>30% of saturation). At saturation levels rates often drop due to the lack of oxygen necessary for aerobic degradation. Many pesticides are capable of being degraded anaerobically, so this possible mechanism must not be neglected. Soil moisture in the orchard may remain at saturation levels only briefly. Under these conditions the development of an anaerobic microorganism population able to significantly alter pesticide concentration is not likely.

The data of Yaron et al. (1974) shows little or no degradation of azinphosmethyl for both sterile and non-sterile dry soils. Increased adsorption, due to the dry conditions, may be partially responsible for the observed results. At 50% of saturation, the degradation rate for the non-sterile soil at 25°C was twice that of the sterile soil. No other data was found in the literature on the relationship between azinphosmethyl degradation and soil moisture. As microbial degradation has been shown to be the primary pathway

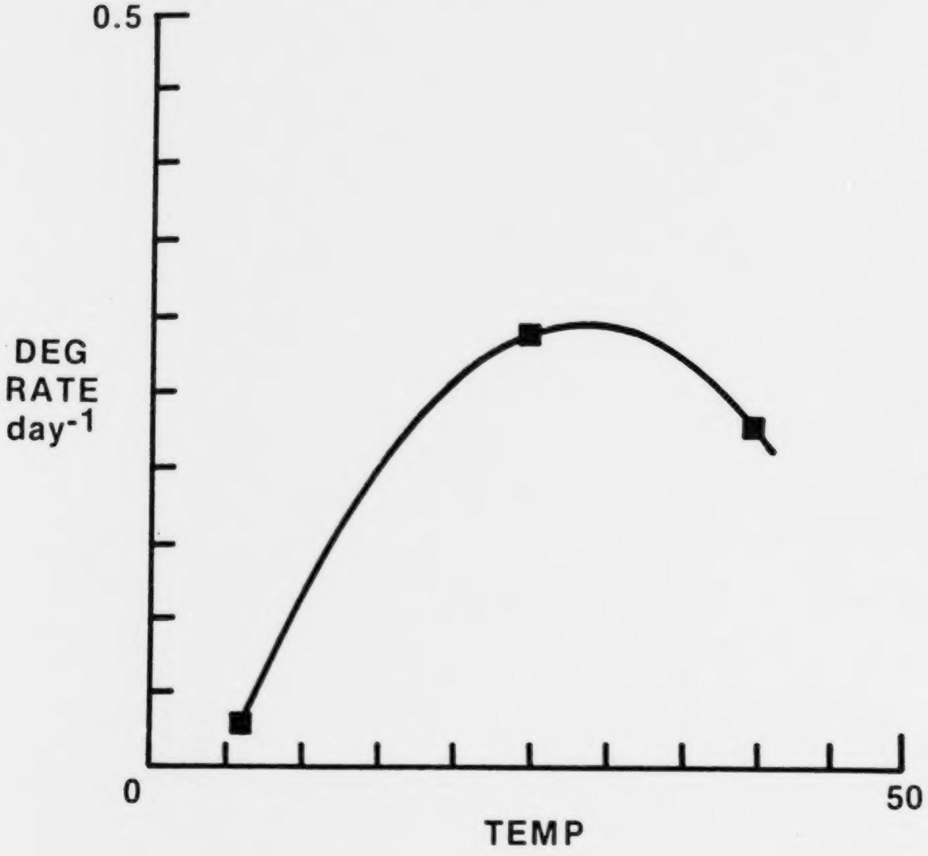


Figure IV-5. Azinphosmethyl Microbial Degradation Versus Soil Temperature

of amitrole loss in soils (Kearny and Helling, 1969), the treatment by Hamaker (1972) of the data of Day et al. (1961) for amitrole is presented as a crude estimate of the influence of soil moisture on azinphosmethyl microbial degradation (Figure IV-6).

The effect of both soil moisture content and temperature on the degradation of a number of herbicides was examined by Walker (1974, 1976a, 1976b, 1976c), Smith and Walker (1977), and Walker and Smith (1979). In these studies no distinction was made between chemical and biological degradative pathways. In all cases a positive correlation was observed betwen the degradation rate and both soil moisture content and soil temperature. These data were used to develop and test a model for herbicide persistence. Assuming first-order kinetics, herbicide half-life as a function of soil moisture was represented by the following empirically derived equation (Walker, 1974):

$$H = am^{-b} \qquad \text{(IV-5)}$$

where H is the herbicide half-life, m is the soil moisture content, and a and b are constants. The Arrhenius equation was used to represent the effect of temperature on the degradation rate. Herbicide persistence in the field was estimated from these two equations using both laboratory determined values and simulated seasonal and diurnal soil temperature and moisture flux (Walker, 1974; Walker and Barnes, 1981). The model was tested against herbicide loss when applied to bare soil, and the model worked best when the herbicide was incorporated. Applicability to cropped fields and particularly perennial crops such as orchards lies in the ability of the model to represent the effects of the crop and/or ground cover on soil temperature and moisture flux. The model in its present state does not have this capability. Further development to represent the effect of soil moisture and temperature on chemical and biological degradative pathways individually would also be desirable.

pH and soil texture may also be important factors influencing microbial degradation. Soils with extremes in pH will most likely have developed microbial populations adapted to these conditions. The influence of pH might be more important, however, if a soil amendment which drastically alters the soil pH is used, thereby requiring adaptation by the microbial community. Soil texture describes the soil aggregate size and the pore space of the soil, which may influence the availability of moisture and air to the microbial population. The interrelationship between all soil properties and the microorganism population must be considered in assessing pesticide degradation.

Photodegradation

Solar radiation is known to be important to the attenuation of pesticides in the environment, as it supplies thermal energy which influences pesticide volatilization and the rate of many degradative reactions. The energy of the photons may also be adsorbed by the bond (electronic) energy of the molecule, which may result in transformation. Much research has been done in the laboratory on the photolysis of pesticides and the photoproducts formed (Zabik et al., 1976). Only recently have attempts been made to determine rates of photodegradation under natural conditions. The most promising approach uses computer modeling techniques to extrapolate laboratory findings to field conditions (Zepp and Cline, 1977). These authors have attempted to predict photolysis of a number of compounds in the aquatic environment. The study of photolysis in solution is preferred as the homogeneity of this medium allows the researcher to accurately monitor and vary the chemical environment.

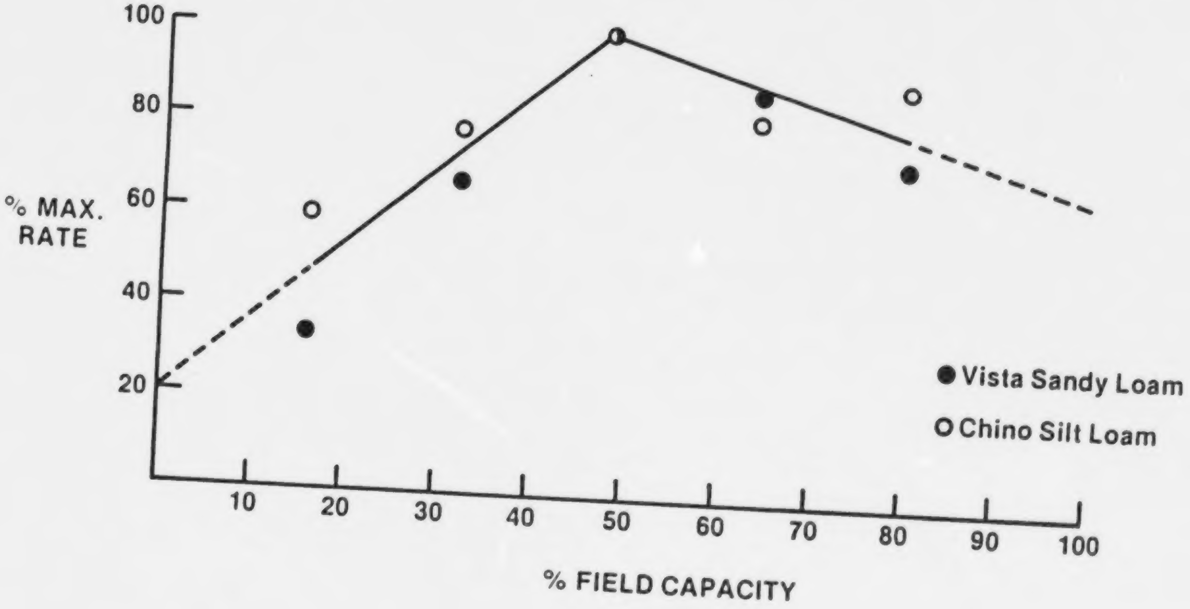


Figure IV-6. Amitrole Degradation Versus Soil Moisture for Two Soil Types

Experiments to determine the photochemistry of compounds in the solid or sorbed state, such as pesticides applied to the soil and plant surfaces, are far less manageable (Zabik and Ruzo, 1981). Relatively few studies have attempted to determine the rate of photolysis on plant and soil surfaces under natural conditions. One of the major difficulties associated with this kind of study is differentiation between photodegradation, volatilization, and metabolism. In addition, the presence of sensitizers and quenchers may greatly alter the rate of photolysis determined in the absence of these substances. For Example, Liang and Lichtenstein (1976) reported that following an eight-hour exposure to sunlight, 2.8% of the ^{14}C azinphosmethyl applied to bean leaves was determined to be the oxygen analog, whereas no oxygen analog was found for applications to corn leaves or glass plates. No oxygen analog was present in the dark controls. The author suggest that a component of the bean leaf may have enhanced the formation of azinphosmethyl oxon in the presence of sunlight. Ninety-three, 88, and 94% of the radiocarbon was recovered from the glass, corn, and bean leaf dark controls. In all cases, the radiocarbon recovered was determined to be unaltered azinphosmethyl. Sixty-six, 86, 72% was recovered from the glass, corn, and bean leaves following the eight-hour sunlight exposure with 5.7, 8.9, and 4.3% of that recovered determined to be photoproducts, based on differential extraction and thin layer chromatography. Substantial loss to volatilization of azinphosmethyl on glass and foliar surfaces as a result of the sunlight exposure is indicated. The greater volatilization of the azinphosmethyl on exposed surfaces, as compared to the control (covered with black cloth), may have been due in part to higher temperature and greater air exchange at the foliar surface. Volatilization of photoproducts must also be considered. It it is assumed that only a small amount of the photoproducts are lost to volatilization, then a crude estimate of the initial rate of photolysis can be made from the percent of photoproducts formed.

As the eight-hour exposure period (0900 to 1700 hr) used by Liang and Lichtenstein (1976) represents only a portion of the daily solar radiation exposure during the summer months in North America, the relationship between the photolysis rate of carbaryl and time of day (July) reported by Zepp and Cline (1977) was used to estimate the initial daily loss rate. Based on the relationship reported by these authors it was assumed that the peak rate of photolysis occurred at approximately 1300 hr, that no photolysis occurred before 1600 hr or after 2000, and that the loss rate varied linearly between the end points and the peak. Integrating the area under the triangle formed yields an estimate that exposure to sunlight between 9099 and 1700 hr is responsible for approximately 82% of the daily loss due to photolysis, during the summer months. The amount of photoproducts formed (estimates of azinphosmethyl loss due to photolysis during the eight-hour exposure), as a percent of dose applied to each surface, was adjusted accordingly to arrive at an estimate of azinphosmethyl initial daily loss due to photolysis. The initial daily loss rates calculated were 6.9, 10.8, and 5.2% day^{-1} for azinphosmethyl on glass, corn, and bean leaves, respectively. The azinphosmethyl degradation rate for dislodgeable residues on apple foliage and the orchard grass determined in Chapter II was approximately 4.5% day^{-1}. The initial daily losses due to photolysis, as determined above, would indicate that photolysis may contribute significantly to the disappearance of azinphosmethyl foliar deposits.

The data of Liang and Lichtenstein (1976) also indicated that azinphosmethyl on the soil surface undergoes photodegradation. Estimated daily initial rates of photodegradation for the three soil types used (sand, loam, muck) were slightly faster than those estimated for the glass and foliar surfaces.

Factors that must be considered when estimating direct photolysis under natural conditions are discussed by Zepp and Cline (1977) and Smith et al. (1977). These include: the incident light intensity, as a function of season, latitude, time of day, cloud cover, percent of light adsorbed by the pesticide (as compared to its surroundings) and qunatum yield (fraction of photons adsorbed that results in transformation). As many pesticides show maximum adsorbance in the ultra violet region, outside the range of wavelengths reaching the surface of the earth, sensitized reactions are often important to pesticide photodegradation. A sensitizer adsorbs, light at a wavelength present, followed by an energy transfer to the pesticide (Khan, et al., 1974). The components of a plant surface which may act as sensitizers are largely unknown.

Rate of Photolysis in the Field

Rates of photolysis on foliar surfaces and soil, as a function of compound properties and environmental parameters, are estimated in the predictive model using the approach for predicting direct photolysis in natural waters proposed by Zepp and Cline (1977). They report that for those situations where the substrate concentration is low and the substrate plus this matrix adsorb less than 5% of the incident light the rate of direct photolysis can be represented by the following equation:

$$\frac{ds}{dt} = K_a \phi [s] \qquad \text{(IV-6)}$$

where K_a = Rate of light adsorption = $2.303/J\Sigma I_\lambda \varepsilon_\lambda$ (Photons m^1 cm^3 s^1)

ϕ = Quantum yield (m/Einstein or molecule/photon)

s = Substrate concentration in m/l

K_a is determined by summing the product $I_\lambda \cdot \Sigma_\lambda$ for the adsorption range of the substrate. I_λ is the light intensity (photons cm^{-2} s^{-1}) and wavelength λ and ε_λ is the molar extinction coefficient (m^{-1} cm^{-1}) of the substrate at wavelenth λ. J is a conversion factor making the units of I_λ and ε_λ compatible (see Zepp and Cline, 1977, for a more detailed discussion). In natural systems where the substrate concentration is low, K_a is independent of substrate concentration and the daily photolysis rate can be estimated from the following equation.

$$K_p = K_a \cdot \phi \cdot A \cdot D \qquad \text{(IV-7)}$$

The A term takes into account the effects of adsorbers or quenchers which may produce the observed rate of photolysis in natural systems and sensitized reactions. At the present this term is set at unity. D is a factor that converts the instantaneous photolysis rate at midday to a daily rate, based on the diurnal variations in solar radiation intensity. D is estimated to be 2.52×10^4 for the summer months at a latitude of 35°N (based on the data of Leighton, 1961). This value for D is used when the midday rate is represented as SEC^{-1}.

To estimate K_a for azinphosmethyl the ε_λ data for parathion presented by Smith et al. (1977) and the $I_\lambda(\omega_\lambda)$ data given by Zepp and Cline (1977) were used. This yields an estimate for $K_a \simeq 10^{18}$. In the predictive model it is assumed that only a portion of the daily overall attenuation rate is due to photolysis. For azinphosmethyl applied to the tree leaves, the daily photolysis rate is arbitrarily set at .018 or 37% of the overall daily attenuation rate. Substituting this value into equation (2), the remaining unknown term, the quantum yield ϕ, must be $\approx 10^{-2}$. It must be understood that Eq. 2 is a simplified form representing a very complex phenomenon. It is hoped that the crude estimates used in this equation are in error by no more than two orders of magnitude. Nevertheless, understanding its limitations, equation (2) allows the user to vary the rate of photolysis based on both environmental parameters $(I_\lambda, A, 0)$ and compound properties $(\phi, \varepsilon_\lambda)$.

Volatilization

In the present form of the predictive model the rate of pesticide airborne loss is fixed and may not vary with environmental conditions. This is certainly not the case in the environment as it has been suggested that windspeed, rainfall, and solar radiation influence the rate of volatilization and erosion of pesticide deposits (see Chapter III). Too little is known about the influence of these parameters to propose even the crudest of equations. Proper representation of airborne loss is further complicated as the rate of loss is far from being first order, for as the surface deposits are depleted the airloss rate decreases rapidly. A more detailed discussion of this phenomenon may be found in Chapter III. Airborne loss is presently represented as an average rate over the sampling period. This badly underestimates the initial loss rate within the first few days after application, and overestimates the rate towards the end of the sampling period. The volatization rate for the tree leaves is 40% of the overall attenuation rate. The user is allowed to vary the volatilization rate based on compound properties using Hartley's equation:

$$FB = \frac{PB(mB)^{1/2}}{PA(mA)^{1/2}} \; FA \tag{IV-8}$$

where: FB = volatilization rate of new compound 'B';
PB = vapor pressure of compound B;
mB = molecular weight of compound B;
FA = volatilization rate of reference compound 'A';
PA = vapor pressure of compound A;
mA = molecular weight of compound A.

For best results the vapor pressure of the new compound "B" should as close as possible to the reference compound A. This will give a rough estimate of the mean rate over A the sampling period. Unfortunately the rate at which the new compound dissipates due to other loss processes may have a profound effect on the actual field airloss rate.

Plant Uptake

Greenhouse studies on plant uptake and metabolism of ^{14}C azinphosmethyl applied to bean leaves (Steffens and Wieneke, 1976) suggest that this loss mechanism may be an important pathway in the attenuation of foliar deposit residues in an apple orchard. The influence of environmental factors such as solar radiation, temperature, humidity and other conditions influencing leaf wetness on plant uptake of pesticides is discussed by Hull (1970), Steffens and Wieneke (1975) and Bukovac (1976). However, no quantitative relationships are presented. A computer model for foliar uptake of pesticides was reported by Bridges and Farrington (1974). This model represents plant uptake by both diffusion and mass flow through the observable structure of a wheat leaf. The model structure does not allow for the influence of environmental conditions on the rate of foliar uptake. A general lack of data in the literature points to the need for further research to investigate the contribution of plant uptake and metabolism to the overall attenuation of foliar residues as a function of environmental conditions. Plant uptake is not represented as a separate attenuation process in the current predictive model, due to the scarcity of data.

The Pesticide Movement Matrices

In Chapter II, a set of matrices was derived to describe the movement of azinphosmethyl among various orchard regions. Matrix P described movement during 24 hours of dry conditions, L described additional movement due to light rain at some time during the 24 hours, and H, movement due to heavier rain. All of these matrices were parameterized using field data collected during 3 seasons of azinphosmethyl spray applications. However, the proportion of the residue in one layer moving to any other layer obviously depends on many factors, including age of residue, formulation, method of application, properties of the active ingredient, material on which the residue is deposited, and environmental conditions. Much laboratory work will be required in order to learn the influences of all of these factors, although they have been studied in many laboratories. However, the mathematical technique by which the influences of these factors, as they are learned, may be incorporated into the model framework presented here is described below.

The movement matrices P, L, and H are each lower-triangular and column-stochastic. An entry H_{ii}, for example, is the proportion of pesticide that remains in region i during one day (a first-order loss under fixed conditions is assumed). H_{ij}, j>i, represents the proportion of pesticide that enters (and remains in) region j from region i during one day. If laboratory studies indicate that a different formulation, for example, washes off region i at a rate r times faster than the currently modeled formulation under heavy rainfall, an adjustment to the ith column of the H matrix can be done based on the assumption that the continuous process underlying the daily loss proportion is:

$$\frac{dC_i}{dt} = -k_i C_i(k) \quad t>0, \qquad \text{(IV-9)}$$

where $C_i(t)$ = pesticide residue in (on) region i at time t, and k_i = instantaneous loss rate (da^{-1}) of pesticide from region i to the lower regions. Then, converting H_{ii} into an instantaneous loss rate, $k_i(da^{-1})$,

$$H_{ii} = e^{-k_i}, \text{ or } k_i = -\ln_e(H_{ii}) \qquad \text{(IV-10)}$$

Thus we can write

$$k_i' = rk_i, \text{ where } k_i' \text{ is the new loss rate. Then} \qquad \text{(IV-11)}$$

$$H_{ii}' = (H_{ii})^r, \text{ where } H' \text{ is the new movement matrix.} \qquad \text{(IV-12)}$$

Remaining entries in column i of H' can be calculated if the pesticide moving out of region i is assumed to be distributed among the lower layers in the same relative proportions as it was in H:

$$H'_{ji} = \frac{H_{ij}\ (1-H'_{ii})}{1 - H_{ii}}\ ,\ 4 \geq j \geq i. \qquad \text{(IV-13)}$$

Specification of the Attenuation Parameters

The field-determined attenuation matrix A is based upon field conditions encountered during three seasons, and represents average total daily attenuation for each layer under those conditions. These daily attenuations, as developed in Chapter II, are presented in Table IV-2, re-arranged from a diagonal matrix into two rows (canopy and alley). The user of the model can change these entries at will. It is possible to further decompose these losses according to the individual chemical and biological processes which were described in the preceding sections. Table IV-3 shows the attenuations separated by process, where each row represents a process. Thus, the entries in each row correspond to the diagonal entries of one of the attenuation component matrices A_m, A_h, A_p, A_v, and A_o. (Surface penetration and plant uptake are considered separately.) Table IV-3 is used only as a starting point for calculating daily losses in the model. If the user alters the overall attenuation matrix A (Table IV-2), entries in Table IV-3 directly, the entries are simply summed to produce a new Table IV-2.

Each process in Table IV-3 is affected by various environmental and compound-specific properties. The model contains factors which can increase or decrease the rates shown in Table IV-3 on a daily basis, depending on environmental conditions (temperature, pH, soil moisture, and soil percent organic matter). These factors are based upon the equations described earlier in this chapter. The user can also modify any of the coefficients used in these equations to incorporate additional information or represent other compounds or conditions. Changes in these multiplicative factors affect the daily rates of attenuation, but are not shown in Table IV-3 which represents only rates under standard conditions. The standard conditions for Table IV-3 are: Air temperature, 23°C; soil temperature, 23°C; soil pH, 7; soil organic matter, 6%; soil moisture, 30% W/W or 50% field capacity; azinphosmethyl as 50% w.p.; vapor pressure, 10^{-7} mm Hg; molecular weight, 317.

Values presented in Table IV-3 were not directly determined experimentally. Rather, they represent our best estimates of the relative contribution of each of these processes to the observed attenuations of azinphosmethyl of Table IV-2. Clearly, intensive laboratory and field work aimed at estimating under natural conditions is required. Such information is now largely unavailable. As values are determined in the future, they may be entered directly into the model.

TABLE IV-2. DAILY AZINPHOSMETHYL ATTENUATION PROPORTIONS, UNDER STANDARD CONDITIONS, SUBJECT TO USER ALTERATION.

	LEAVES	GRASS	LITTER	SOIL
CANOPY	.0487	.0412	.0412	.0790
ALLEY		.0670	.0670	.0790

TABLE IV-3. DAILY AZINPHOSMETHYL ATTENUATION PROPORTIONS, SEPARATED BY PROCESS, UNDER STANDARD CONDITIONS, SUBJECT TO USER ALTERATION.

	CANOPY				ALLEY		
	LEAVES	GRASS	LITTER	SOIL	GRASS	LITTER	SOIL
MICROBIAL DEG.	0.000	0.000	.010	.070	0.000	.017	.070
HYDROLYSIS	.012	.012	.015	.009	.019	.025	.009
PHOTOLYSIS	.018	.006	.003	0.000	.010	.004	0.000
VOLATILIZATION	.019	.024	.013	0.000	.038	.021	0.000
OXIDATION	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Penetrated Residues

Surface-penetrated residues (as defined in Chapter I) consist of residues on or within the cuticular matrix of tree leaves, grass/broadleaves, and litter/moss layers. These residues, together with all pesticide residues in soil, will be called "penetrated" residues in the remainder of this report. All dislodgeable pesticide residues which enter soil become "penetrated," but there is no daily penetration process, and attenuation of soil residues is included in the attenuation matrices already presented. Three processes are modeled in representing all other penetrated residues: (1) initial penetration on the day of pesticide application, (2) daily penetration of a proportion of the dislodgeable residues in each layer and region, and (3) daily attenuation of a proportion of the current penetrated residue in each layer and region.

Initial penetration was estimated from field data as presented in Chapter I. Little is known about the time-course of penetration of dislodgeable residues following pesticide application, although it is known that pesticide leaf uptake may vary with pesticide, formulation, mode of application, amount applied, leaf type, and environmental conditions (Hull, 1970). Our field-determined ratios of dislodgeable to surface-penetrated residues in each layer showed a large daily increase in penetrated residues in the litter/moss layer. From these limited field data, the estimated daily penetration rates for the litter/moss layers were .126 and .156 for canopy and alley litter/moss, respectively. In contrast, no daily trend in penetration within tree and grass/broadleaf layers was discernable, and the model's default daily penetration rates for these layers are set to zero.

Due to the dearth of information on attenuation of penetrated residues, the default daily attenuation proportion of penetrated residues was arbitrarily set at 1%/day for all (non-soil) penetrated residues.

Results and Discussion

A series of runs of the model were made in order to examine the effects of various modeled processes on the dynamics of the pesticide azinphosmethyl. Each of these runs is compared graphically with a standard run in which all parameters are at their default values, and wind speeds, temperatures, rainfall, and spray applications are set to represent the 1978 season in our orchard (see Chapters II and III). Daily temperature and soil moisture effects on the various attenuation rates are included in the solid lines (the "base line run") of Figure IV7, but are exluded from the dashed lines, which are based on the standard condition attenuation rates of Table IV2.

Each graph shows one layer's daily azinphosmethyl dislodgeable or soil residue as μg/cm^2 ground area versus Julian date for the 1978 spray season (for a definition of the layers and regions, see Chapter I). Note that leaf surface residues were converted from μg/cm^2 leaf area to μg/cm^2 ground area based on estimates of leaf surface area/tree described in Chapter I. Dates and amounts of rainfall are indicated by arrows above the graph, whil pesticide application dates are shown by arrows below (see Chapter III).

In Figure IV-7(a), the characteristic decline of pesticide level following each spray is observed in the tree. After heavy rains, an even steeper decline is evident. The relative lack of effect of temperature on attenuation in the tree is visible in the overlapping of the solid and dashed lines. This reflects the lack of temperature effects in our photolysis and volatilization submodels, and the relative unimportance of hydrolysis in this layer.

Similar patterns are observed in the grass/broadleaf layers (Figures IV-7 (b) and (e)). Note that while rainfall washes residues from trees to grass, it washes even more out of the grass layer, resulting in a net decline in grass/broadleaf residues after rainfall. Again, temperature effects in the model are minimal on this layer.

The litter/moss layers (Figures IV-7(c) and (f)) are net recipients of pesticide residues following rain events. Temperature effects are more pronounced in this layer, although they are still not striking.

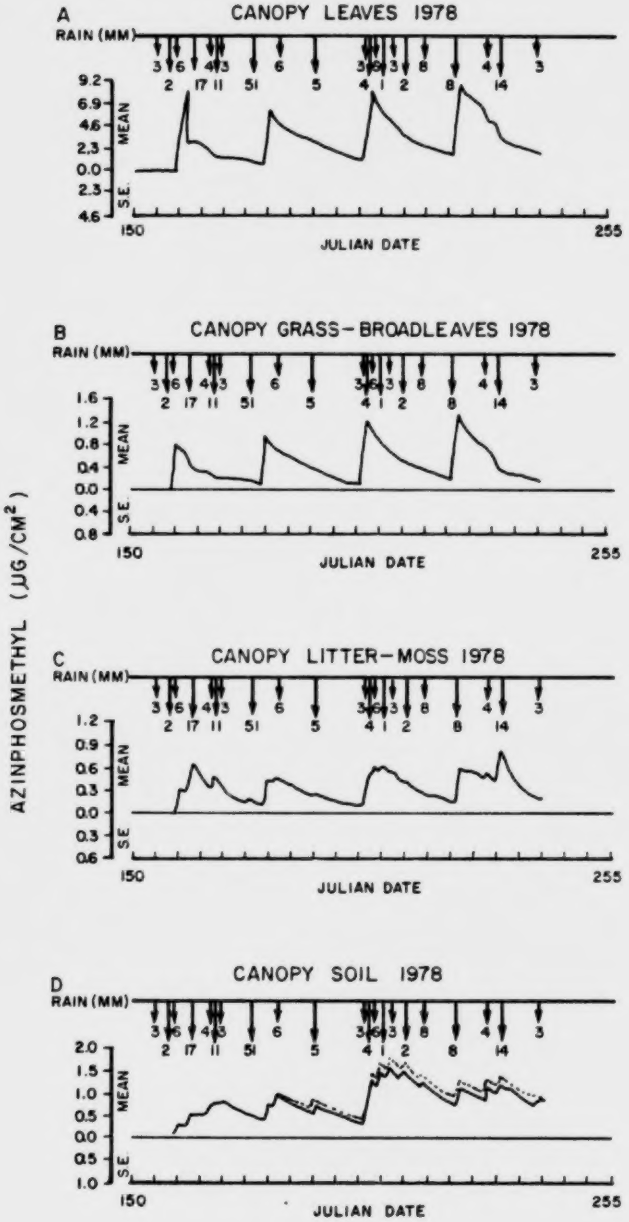
In the soil layers, the influence of daily temperature changes on the microbial degradation rate is evident, as shown in Figure IV-7(d) and (g). The warmer-than-standard temperatures later in the season resul in lower levels of soil residues than under standard conditions.

Figure IV-8(a-d) compares residues from the run using field-determined daily temperatures (the baseline run of Figure IV7) with residues from a run in which daily temperatures are lowered by 10°F (dashed lines). Temperature effects on the residue levels in the tree and grass/broadleaf layers were barely discernable, and are not shown. Greater effects are observable in the litter/moss and soil layers, which show higher residue levels at the lower temperatures, attributable to the temperature effects on microbial degradation in these layers.

Figure IV-9(a-d) shows the effect (dashed lines) of increasing the volatilization rate by a factor of 10 (from 10^{-7} to 10^{-6} mm Hg). This change in volatilization rate is small relative to the range of volatilization rates commonly observed for pesticides. However, the model predicts a pronounced decrease in residue levels in all layers. Especially interesting is the indirect effect on soil residues, from which the model does not postulate any volatilization (using its default parameters). Thus, in the soil, the reduction is solely attributable to lowered availability of residues from upper layers.

Figure IV-10 shows the effect (dashed line) of altering soil pH from 7 to 9 in the soil layers. This resulted in a marked reduction in residue levels, attributable to an increased hydrolysis rate. Under these postulated, strongly alkaline conditions, the model predicts that hydrolysis in soil is changed from a relatively unimportant process to the dominant cause of azinphosmethyl loss.

Figure IV-11(a-g) shows the predicted effects of a postulated two-fold increase in the daily rates of movement of pesticide residues under rainfall



CANOPY LEAVES 1978

CANOPY GRASS-BROADLEAVES 1978

CANOPY LITTER-MOSS 1978

CANOPY SOIL 1978

Figure IV-7(a-d). Predicted 1978 azinphosmethyl residues in orchard canopy region layers. Dashed lines represent predictions based on standard condition attenuation rates (Table IV-2), while solid lines include predicted effects of daily temperature and soil moisture changes (the "base line run").

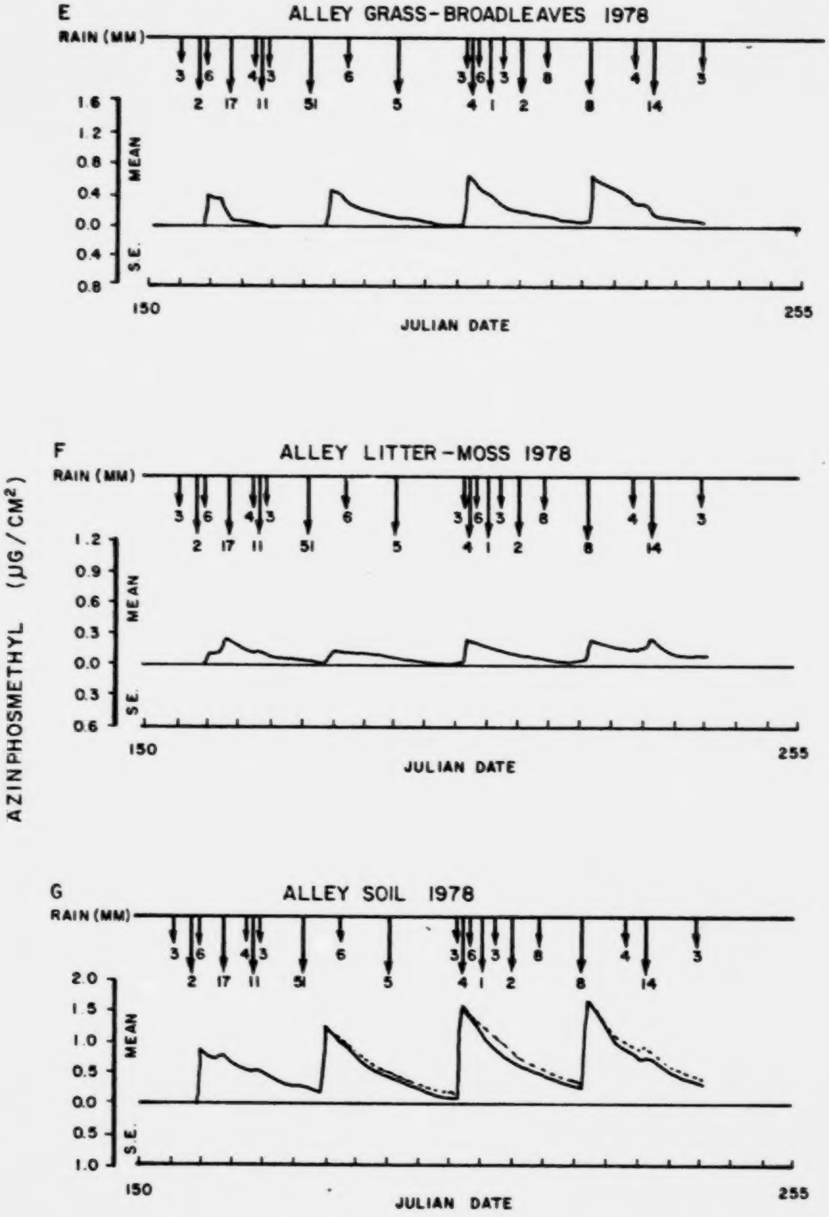
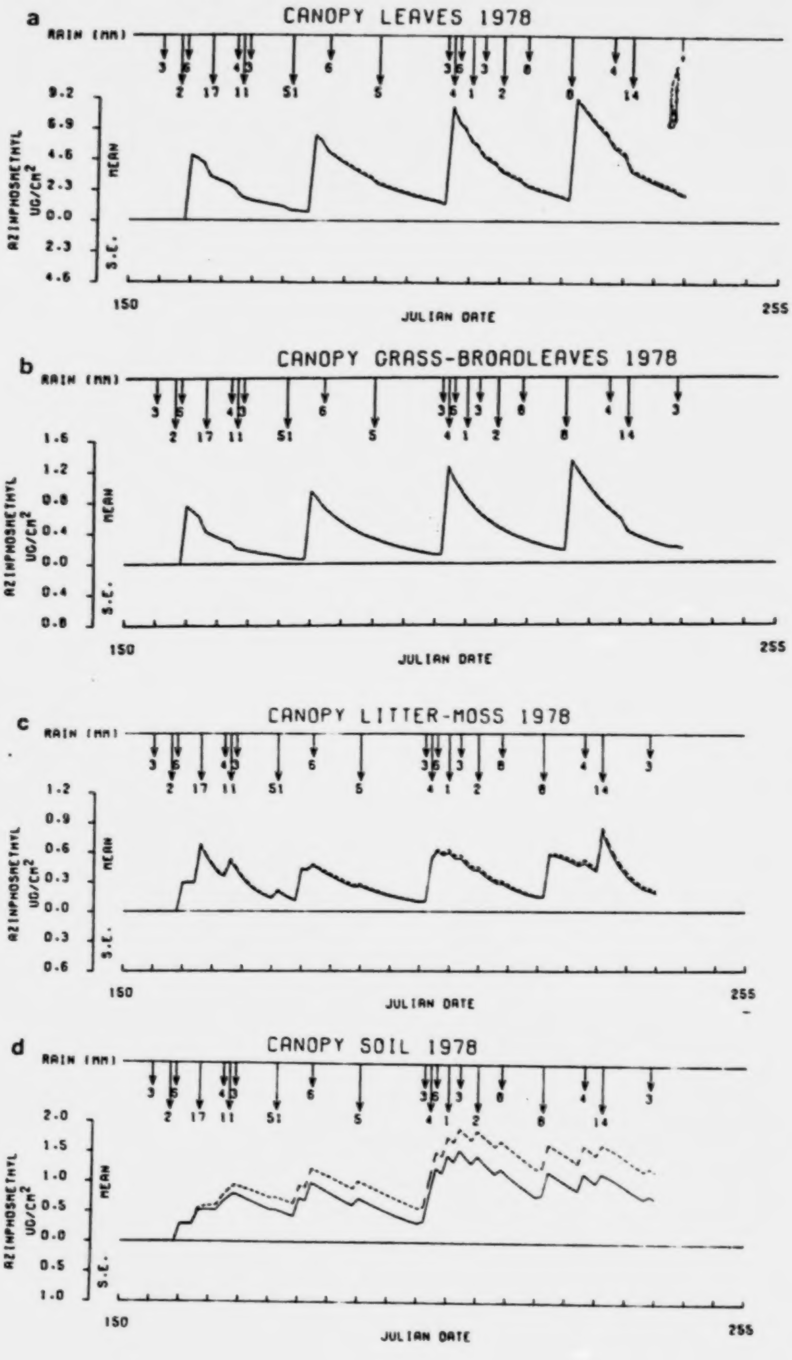


Figure IV-7(e-g). Predicted 1978 azinphosmethyl residues in orchard alley region layers. Dashed lines represent predictions based on standard condition attenuation rates (Table IV-2), while solid lines include predicted effects of daily temperature and soil moisture changes (the "base line run").



a CANOPY LEAVES 1978

b CANOPY GRASS-BROADLEAVES 1978

c CANOPY LITTER-MOSS 1978

d CANOPY SOIL 1978

Figure IV-8(a-d). Predicted effects of lowering daily temperature by 10^{o}F on azinphosmethyl residues (dashed lines) versus the base line run (solid lines).

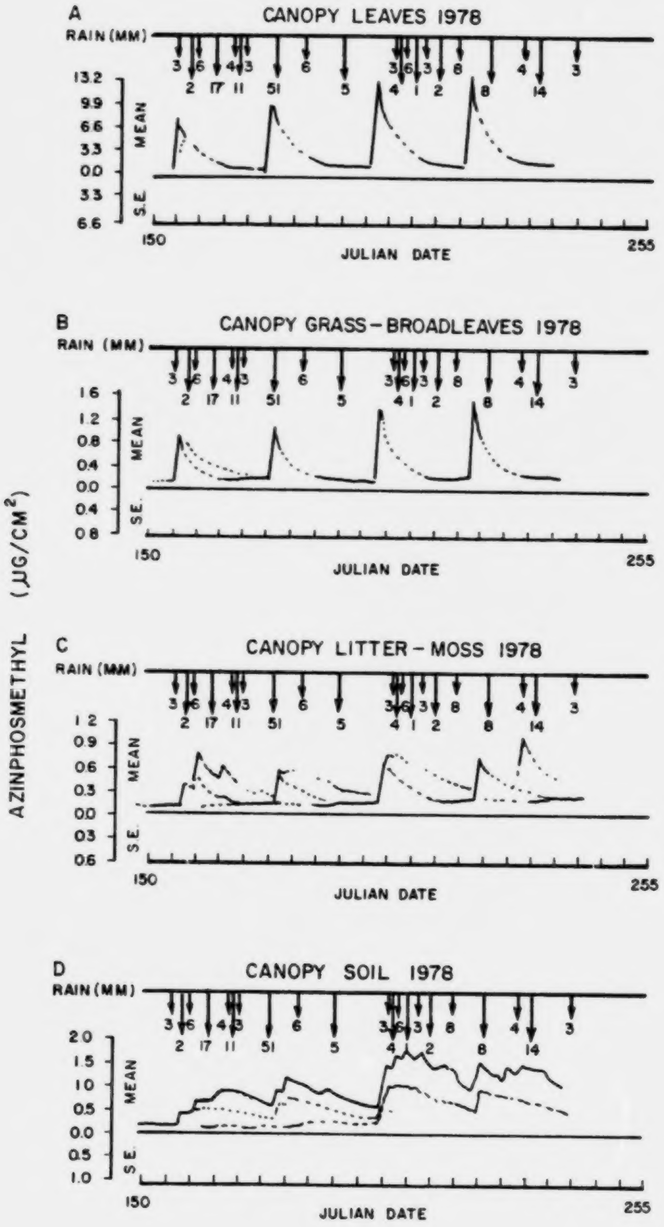


Figure IV-9(a-d). Predicted effects (dashed lines) of increasing pesticide volatilization rate by 10x (from 10^{-7} to 10^{-6} mm Hg). Solid lines are base line run.

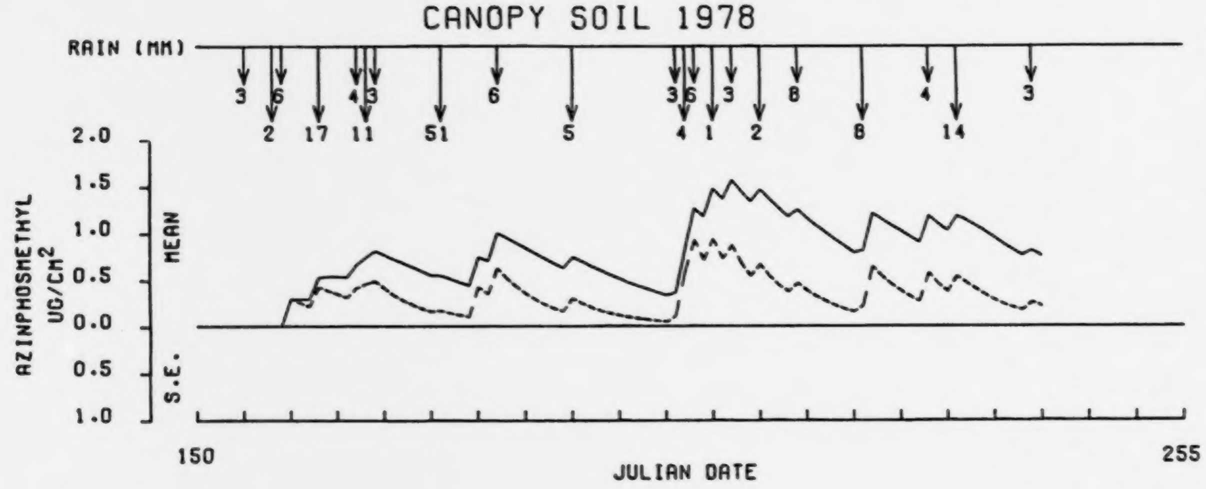


Figure IV-10. Predicted effects (dashed line) of altering soil pH from 7 to 9.

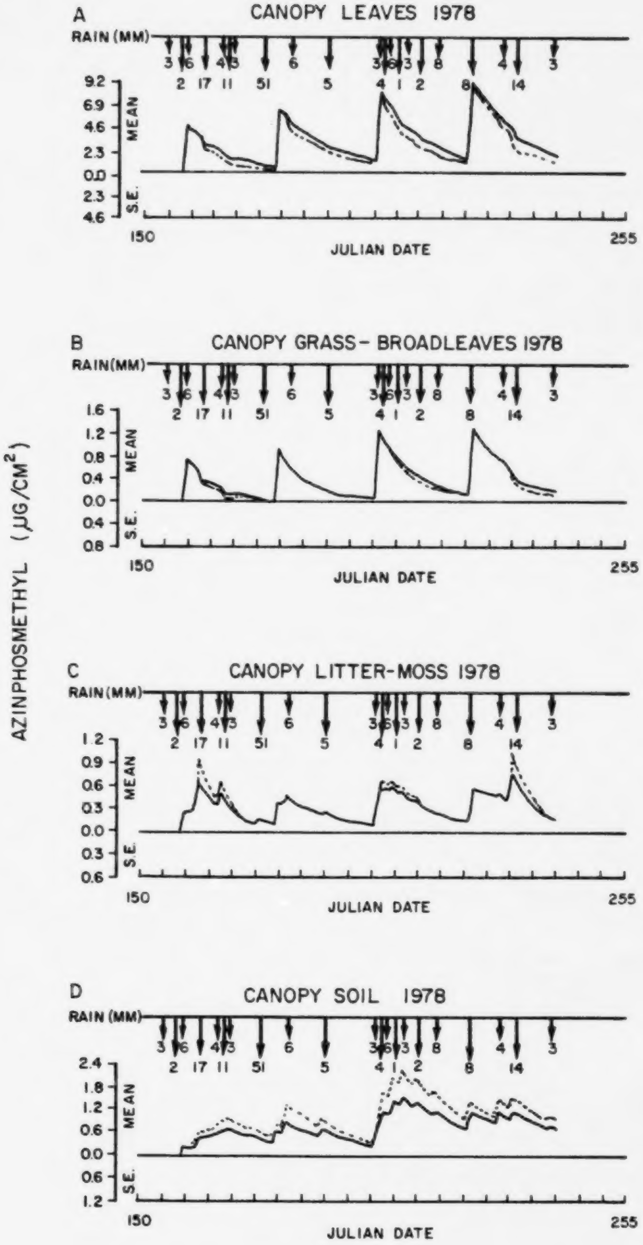


Figure IV-11(a-d). Predicted effects (dashed lines), in canopy layers, of doubling daily rates of pesticide movement due to heavy and light rainfall. Solid lines represent the base line run.

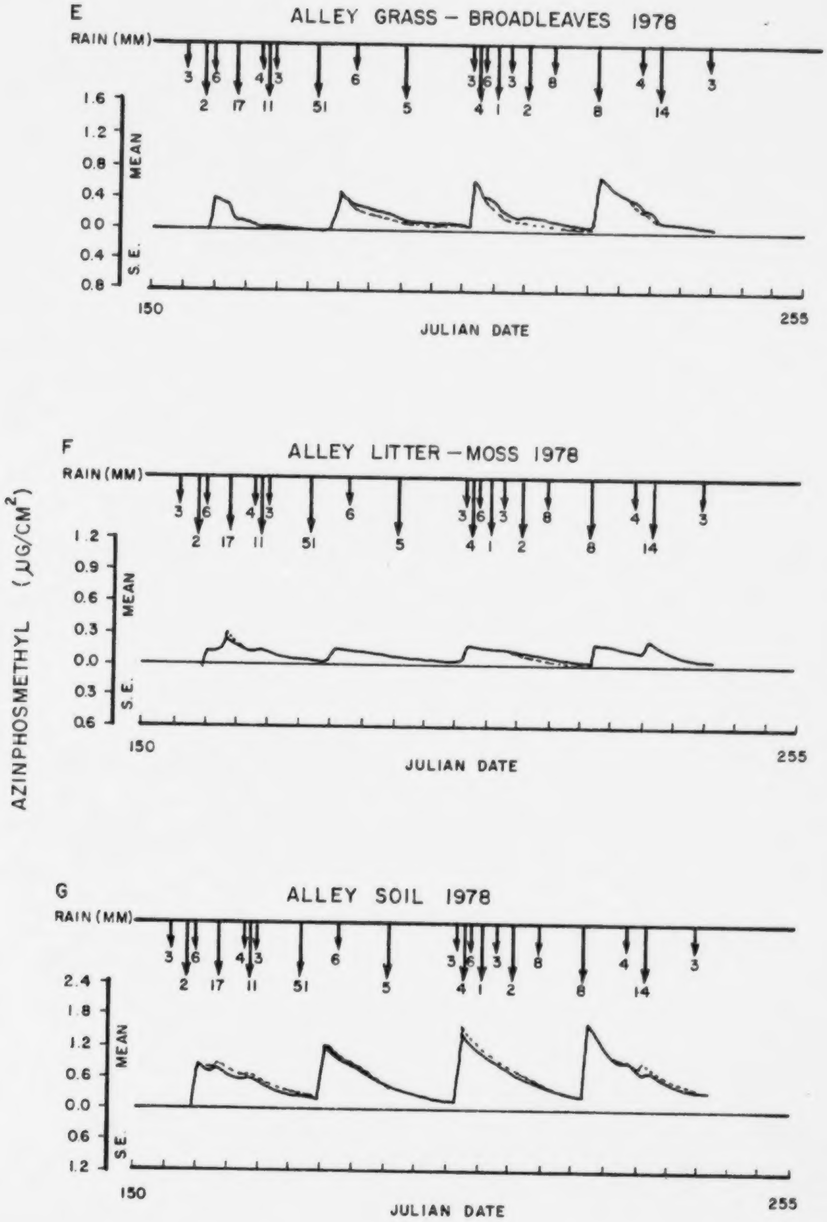


Figure IV-11(e-g). Predicted effects (dashed lines), in alley layers, of doubling daily rates of pesticide movement due to heavy and light rainfall. Solid lines represent the base line run.

conditions (both heavy and light rainfall). Such changes may represent differences in compound properties, formulation, or foliar characteristics. Tree residues are reduced, while grass/broadleaf and litter/moss residues show only slight changes. Canopy soil residues are noticeably increased, while alley soil residues rise only slightly. The relative lack of effect on the grass/broadleaf and litter/moss layers results from the counter-balancing of increased residue movement into and out of these layers, while the soil layers are only recipients of the residues.

Figure IV-12(a-g) shows the effect (dashed lines) of postulating no pesticide movement under non-rainfall conditions. The tree, as expected, shows increased residue levels. The canopy grass/broadleaf residues are higher than "normal," demonstrating that under normal conditions, this layer was a net loser of residues due to non-rainfall movement. Similarly, but to a lesser degree, the canopy litter/moss layer shows an increase in residue levels. Canopy soil, on the other hand, shows a decrease in residue levels, as would be expected, but of a relatively large magnitude. Alley grass/broadleaves shows a smaller increase than the corresponding canopy regions, while alley litter/moss actually shows a considerable decrease in residue levels, since this layer is a net recipient of residues under normal non-rainfall conditions. Alley soil shows little change, as very little pesticide moves into this layer even under normal non-rainfall conditions.

Conclusions

The literature reviewed and the results of the preliminary experiments reported provide a basis for additional work. Further model development, as a method for better understanding of pesticide environmental dynamics, will require the formulation of laboratory and field experiments that are specifically designed to provide data to be used in the quantitative analysis of pesticide fate as a function of environmental conditions. The conceptual model presented identifies the key processes in the assessment of pesticide fate in an orchard ecosystem and the working model provides a framework for further investigation.

Understanding pesticide fate throughout the entire orchard ecosystem is now gaining importance as a result of the interest in integrated pest management as a long-term strategy for pest control. In orchards and many other crops, where chemicals are still heavily relied upon, the success of biological control as a major component of IPM may depend largely on the judicious use of pesticides. The trend in pest management research has been to use modeling techniques to better understand the ecobiology of pest, host, and beneficial species so as to maximize the effectiveness of biological control measures. A comparable effort in modeling pesticide fate and effects on both harmful and beneficial species is essential to the development of effective and efficient orchard integrated pest management programs.

The use of modeling techniques to better understand pesticide fate in orchards may also provide a basis for the development of models describing the fate of organic toxicants in terrestrial ecosystems in general. Ecosystems use energy from the sun to constantly recycle their water, air, mineral, plant and animal resources. Natural mechanisms recognized by ecologists to be essential to these systems include: biogeochemial cycling, host-parasite relations, competition for food and habitat, predator-prey relationships, food chains, symbioses, community-diversity and succession, and natural selection (Odom, 1971; Pimentel and Goodman, 1974; Southwick, 1976; NSF/RA, 1976). The effect of the introduction of chemical substances into the environment

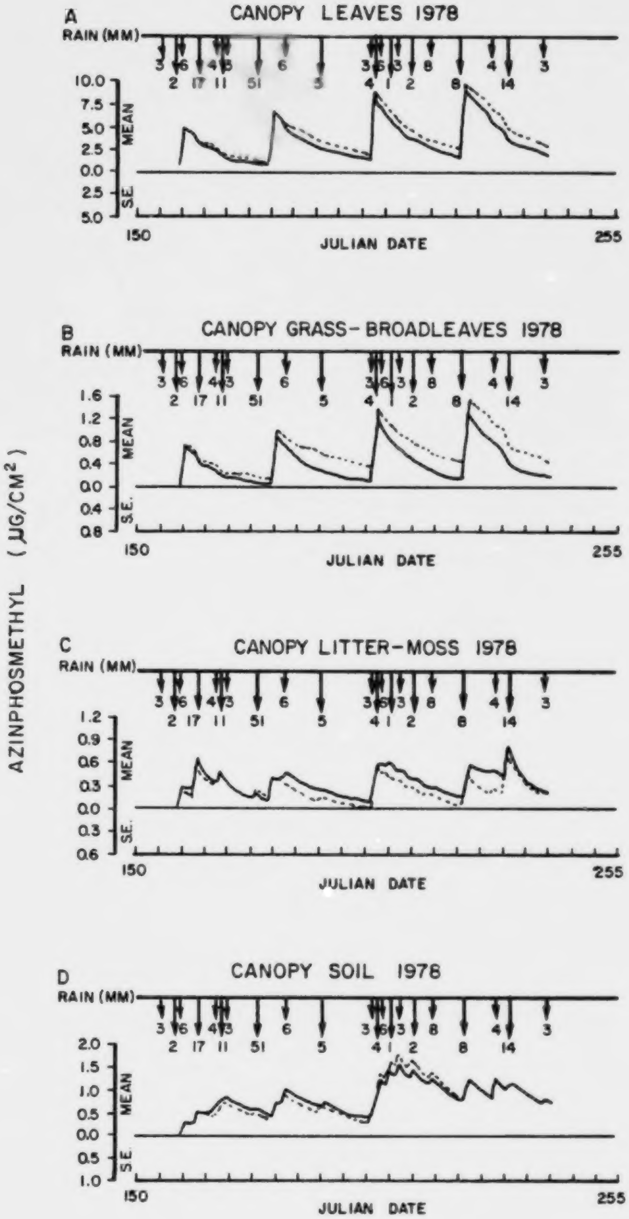


Figure IV-12(a-d). Predicted effects (dashed lines), in canopy layers, of postulating no inter-layer pesticide movement under non-rainfall conditions. Solid lines represent the base line run.

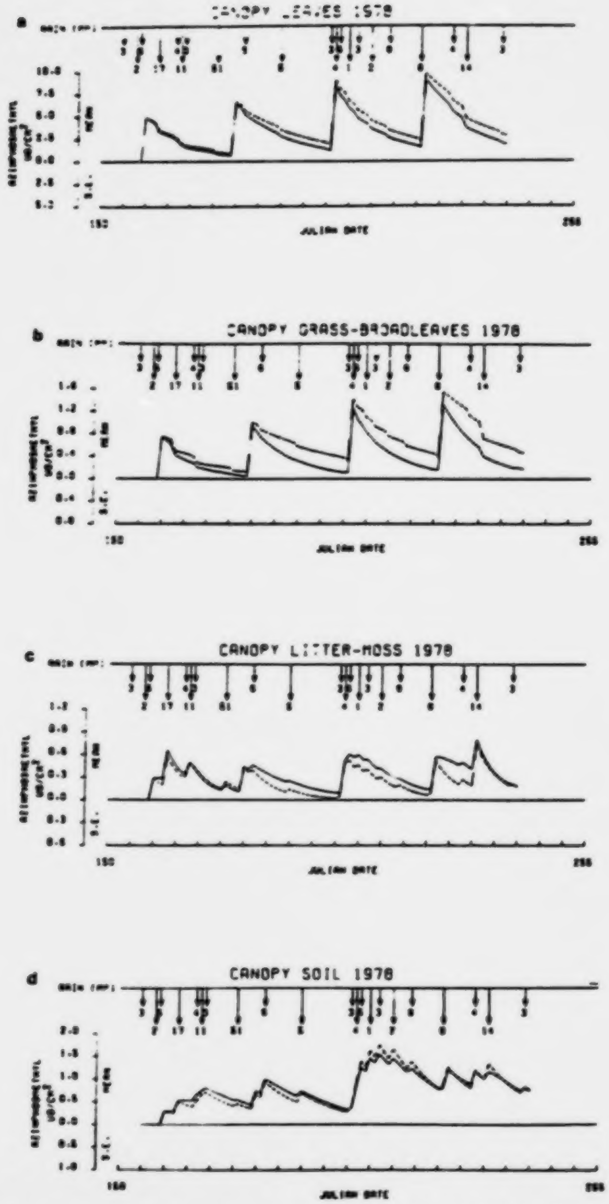


Figure IV-12(a-d). Predicted effects (dashed lines), in canopy layers, of postulating no inter-layer pesticide movement under non-rainfall conditions. Solid lines represent the base line run.

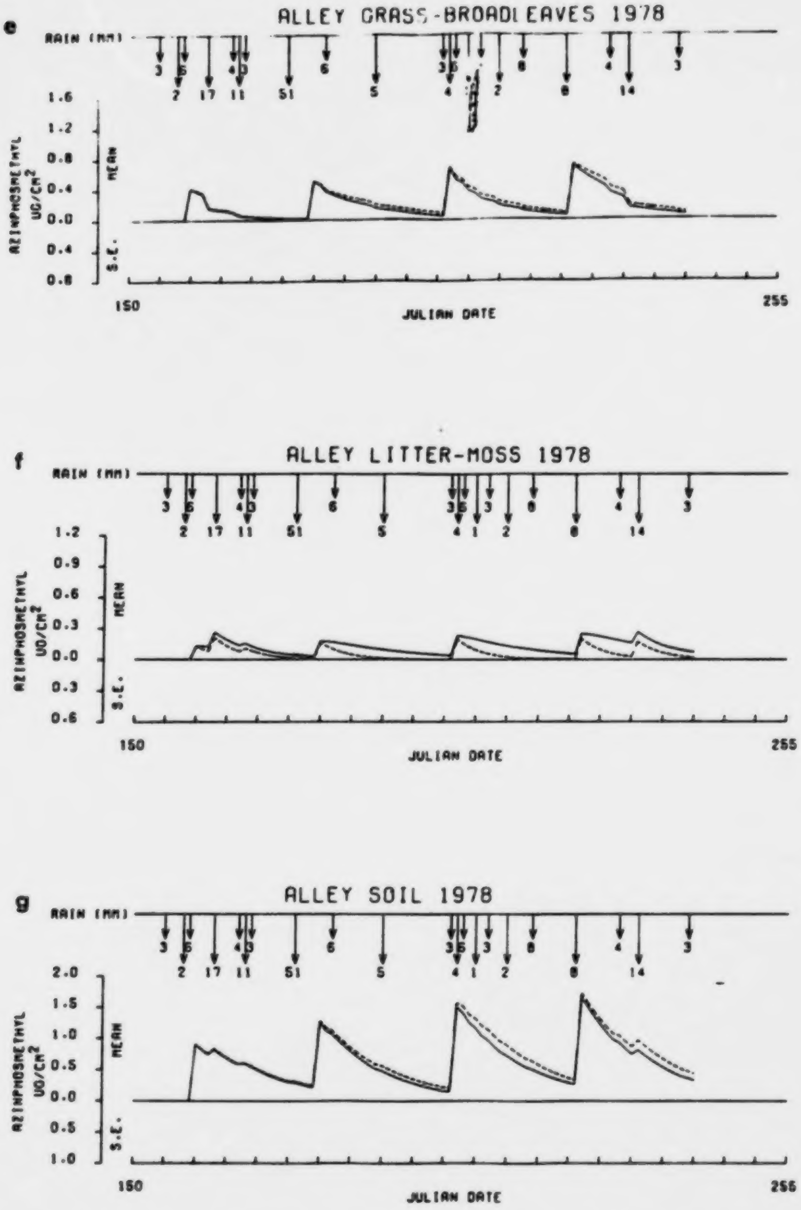


Figure IV-12(e-g). Predicted effects (dashed lines), in alley layers, of postulating no inter-layer pesticide movement under non-rainfall conditions. Solid lines represent the base line run.

on the above-mentioned natural mechanisms of ecosystems is largely unknown. No tests are currently available which can address ecosystem effects at this level. The EPA admits that proposed tests under FIFRA and TSCA are only screening tests and that there is an urgent need for development of higher level ecosystem tests. The question now arises as to whether these screening tests can adequately select those compounds which will most likely pose no hazard to ecosystems. Does a negative result in an acute toxicity test preclude behavioral effects on a population influencing its ability to compete for food and/or habitat? There is no evidence that even chronic toxicity or life cycle studies can give the answer to this question. It is disturbing that negative results for all of the proposed "ecosystem effects" tests may allow continuous low level exposure of a chemical substance when nothing is known about the effects of this exposure on any of the aforementioned "essential natural mechanisms" of ecosystems. A large effort by the scientific community is needed to better understand ecosystem effects above the species level. This effort seems paramount in light of the apparent inability of present screening tests to preclude higher level effects. Rapid development of ecosystem effects test standards should include the use of mathematical modeling techniques to deal with the complexity of the interactions involved. These ecosystem effects models can then be coupled with chemical exposure models producing a very powerful tool in ecosystem hazard assessment. The development of ecosystem models appears to be much farther off than exposure models. In the near future, much emphasis must be placed on rapid development of exposure models, in screening chemicals for ecosystem effects. Accurate predictions of exposure may offset much of the uncertainty in ecosystem effects screening tests.

CHAPTER V

FIELD STUDIES OF AZINPHOSMETHYL (GUTHION®) EFFECTS ON SOIL/LITTER INVERTEBRATES

INTRODUCTION

This chapter summarizes the results of a program of sampling of several invertebrate species in sprayed and control plots over a four-year period. Additional field data for the 1977-78 sampling years for *Trachelipus rathkei* (Isopoda) are presented in Chapter IX, while the 1979 *T. rathkei* field data are included here.

Orchard plots:

The following general description of experimental plots is intended to introduce some of the considerations that will be brought up in the interpretation of field sampling data given in subsequent sections.

Plot size varied from 0.04 to 0.11 hectares; slopes ranged from 6-12% (plots 3 and 4) to 18-25% (plots 1 and 2), and slope direction from North (control 8) all the way to South (plot 4). Soil types were relatively uniform, belonging to the Marlette loam, sandy subsoil series (Soil Conservation

matter.

Differences in tree population can be exemplified by plot 2, where large, dense trees prevailed, and plots 3 and 4 which contained small trees with sparse to medium canopy. Average canopy areas over ground varied from 27% to 54% of plot area. In 1976, the distribution of ground cover types was analyzed in all plots (line intercept technique, Cox, 1974), and a link between tree population and vegetation type became apparent: importance values for ground cover categories (ranging from "bare ground" to more complex categories such as "moss covered by litter and broadleaves") were similar in all plots except plot 2, which harbored the largest, densest trees.

All this implies that vertical and horizontal temperature profiles in soil and litter were equally unevenly distributed. In 1976, temperatures under canopy cover and in alleys were compared on a number of dates: litter surface temperatures differed by up to 15°C, soil surface temperatures by up to 8°C; at a depth of 3 cm, soil temperatures in alleys were up to 5°C higher than under canopy cover.

The orchard was well isolated from commerical orchards in the area. Surrounding habitats consisted of oldfields to the North, an alfalfa field to the South, and small wooded areas and shrubs to the East and West. Although 12" aluminum fencing (buried about 4") partially surrounded the sprayed plots for runoff channeling, the fencing was not continuous around all plot peripheries, and probably presented only a minor obstacle to invertebrate migration.

While most of these physical variables can be taken into account in a model of pesticide distribution and movement, their combined effects on invertebrate populations (including edge habitats as a source of immigrants) often have to remain speculative.

Surface-active invertebrates (1977 to 1979):

Pit-traps containing ethylene glycol were set out for 72 hours at a time, on 8 sampling dates in 1977 and 1979, and on 5 dates in 1978. The total number of traps per plot were assigned equally to locations under canopy cover and in alleys.

Due to priority shifts in the spray program, pit-trap sampling in a given plot was not consistent through the 3 years. Table V-1 provides an overview of the plots sampled.

The trapped faunal material was sorted to order level (Collembola being further subdivided into Arthropleona and Symphypleona), and each year's data for selected groups were subjected to a nested analysis of variance. The statistical models used for analysis were modified to fit the specific sampling plan for each year.

Table V-2 shows results of analysis of variance for those faunal groups that were trapped most consistently and in large enough numbers (at least in control plots) to merit analysis. Significance levels varied considerably from year to year. Seasonal activity or density peaks were reflected in highly significant date effects for all groups. Treatment effect were generally, and unexpectedly, more prominent in 1979 than in previous years, although diazinon application in 1979 was technically not successful. Spiders, which prey on Collembola, may have been affected indirectly: sminthurids, which constituted the overwhelming majority of all trapped Collembola, were significantly decreased in all years.

Effects of other factors and their interactions were so variable as to make valid interpretation virtually impossible. As has been mentioned repeatedly, migration of invertebrates to and from plots could not be prevented, and probably was the major factor responsible for inconsistent results. Overall, the data indicate that this type of investigation would be worthwhile in other locations (such as large, commercially managed orchards) where small-scale population movements would have relatively little effect.

TABLE V-1 PLOTS SAMPLED BY PIT-TRAPPING IN 1977-79

Plot no.	1977	1978	1979
1	not sampled	3rd year guthion, but spraying stopped after June 9	Not sampled
3	not sampled	3rd year Guthion	diazinon after 3 yrs Guthion
4	2nd year Guthion	not sampled	not sampled
6	2nd year Guthion	not sampled	not sampled
7	control	control	diazinon
8	control	control	control

TABLE V-2. Results of analysis of variance of selected groups of invertebrates found in pit-trap samples (NS = not significant; dashes = factors not included in the statistical model in 1979).

	SPIDERS			COLEOPTERA			HEMIPTERA			SYMPHYPLEONE COLLEMBOLA			ARTHROPLEONE COLLEMBOLA		
	'77	'78	'79	'77	'78	'79	'77	'78	'79	'77	'78	'79	'77	'78	'79
Tmt	.1	.05	.01	.1	NS	.001	NS	NS	.001	.1	.05	.001	NS	NS	.001
Plot(tmt)	.005	NS	-	.025	.001	-	.001	NS	-	.001	.001	-	NS	.05	-
Location	NS	NS	.005	NS	NS	.001	NS	NS	.1	.1	.01	.001	NS	NS	.001
Tmt-loc.	NS	NS	NS	NS	NS	.001	NS	NS	.001	.1	.05	NS	NS	NS	.1
Plot-loc.	NS	.01	-	NS	.05	-	NS	.1	-	NS	NS	-	NS	NS	-
Date	.001	NS	.005	.001	.1	.001	.001	.001	.001	.05	.005	.001	.001	.001	.001
Tmt-date	.1	NS	NS	NS	NS	.001	.005	NS	.001	NS	.01	.001	NS	.05	.001
Plct-date	NS	NS	-	.025	.001	-	NS	NS	-	.001	.1	-	.025	NS	-
Loc.-date	NS	.1	NS	.1	.005	NS	NS	NS	.001	.1	NS	.001	.001	NS	.001
Tmt-loc-da	.001	NS	NS	NS	.025	NS	NS	NS	.1	.1	NS	.025	NS	NS	NS
Plot-loc-da	NS	NS	-	NS	NS	-	NS	.1	-	NS	.001	-	NS	NS	-

LUMBRICIDAE:

Methods: Block samples, 25x25 cm, were taken in 10 cm depth increments down to 40 cm in 1976 and to 30 cm in 1977. Each increment was handsorted for worms and coccoons. A preliminary comparison between handsorting and formalin extraction showed that the shallow-burrowing species found in the upper 30 cm (predominantly *Allolobophora caliginosa* Savigny) did not respond to formalin. The deep-burrowing, surface-feeding forms could have been extracted by formalin, but the concurrent disturbance of large plot areas prohibited use of this technique.

A minimum of 3 block samples were taken per plot, twice a year, in June and October. The sampling locations were chosen such that data analysis could take in to account: slope location (up-, mid- and down-slope); location with respect to canopy (under canopy cover vs. in alleys); and sprayed vs. control plots.

Results: The number of worms recovered from samples varied considerably even within one given type of location. Table V-3 shows results of the 1976 season, in which all plots were sampled (June = pre-spray), and of the 1977 season, in which only 4 plots were sampled, and plot 8 (as a second control) was sampled for the first time. Analysis of sample counts from both seasons, combined according to the parameters mentioned above (slope, canopy cover, pesticide and season), did not reveal any significant differences in worm densities, (variances equal, two-sample t-tests, $P > 0.2$ in all cases).

Table V-4 gives a more detailed summary with respect to subsample depth. Two-way analysis of variance showed a significant interaction between Guthion application and depth distribution only in the June 1977 samples ($f = 11.13$, $P < 0.0002$): the uppermost layer in sprayed plots harbored a greater proportion of the total number of worms found than the upper 10 cm in control plots. One should consider, however, that the samples were taken over a period of 2 weeks, under slightly varying weather conditions. In addition, soil texture was not entirely uniform throughout all control and sprayed samples. Statistical significance of this difference is therefore open to several possible interpretations.

Under our experimental conditions, no significant conclusion could be drawn with respect to any of the parameters anlysed, including effects of Guthion in the field. If the pesticide had any effects on the topsoil-dwelling worm species, variability introduced by other habitat features masked them. Thus a reduction in worm populations in June 1977 included those in the control plot (Table V-4); in this case, periodic compaction by mowing and spraying would provide a more plausible explanation for worm mortality (in view of the work by Morris, 1968, Chapell et al., 1971, and Aritajat et al., 1976) than would pesticide effects.

Furthermore, since *A. caliginosa* is a topsoil-dweller, but not a surface feeder (classified as endogée by Bouché, 1972), contact with contaminated orchard floor/strata must be minimal, especially in dry years such as 1976. In laboratory experiments, it has been shown that prolonged exposure of *A. caliginosa* to Guthion will reduce worm weight and coccoon production (van Rhee, 1976). In commercial orchards, which characteristically have heavy spray programs, pesticide effects may be noticeable: van Rhee (1977) documented drastic reductions in *A. caliginosa* populations, but in his study Guthion was only one of several compounds used. Under the comparatively light spray regime used in the present study, Guthion application had no discernible impact on the earthworm population in upper soil layers.

TABLE V-3. Mean number of *A. caliginosa* per sample in 1976 and 1977. Three samples were taken per plot. The figures include all worms found in the upper 30 cm of soil (means ± S.E.)

Plot number	June 1976	October 1976	June 1977	October 1977
1	56.3 ± 0.9	40.0 ± 4.6	38.7 ± 10.8	70.3 ± 12.8
2	55.3 ± 7.1	51.3 ± 9.6		
3	53.3 ± 4.7	27.7 ± 4.4	25.7 ± 1.7	26.7 ± 7.9
4	32.3 ± 9.4	49.0 ± 18.4		
5	25.7 ± 5.9	22.3 ± 2.3		
6	34.6 ± 5.0	38.0 ± 13.3		
7 CON	53.6 ± 13.7	47.3 ± 11.4	23.3 ± 6.9	59.7 ± 20.6
8 CON			39.5 ± 9.3	48.3 ± 3.3

TABLE V-4. Average percent of worms found in 3 depth increments (mean ± S.E., number of samples in parentheses) in the 1976 and 1977 sampling seasons.

	SUBSAMPLE DEPTH		
	0-10 cm	10-20 cm	20-30 cm
June 1976 (all plots)	30.4 ± 3.9 (21)	53.0 ± 3.3 (21)	16.6 ± 2.2 (21)
October 1976 (all plots)	43.3 ± 6.1 (21)	44.5 ± 4.6 (21)	12.2 ± 2.2 (21)
June 1977 (all plots)	61.2 ± 7.9 (15)	32.8 ± 6.7 (15)	6.0 ± 2.1 (15)
October 1977 (all plots)	94.1 ± 1.4 (11)	4.6 ± 1.2 (11)	1.3 ± 0.9 (11)
June 1977 (sprayed)	83.2 ± 6.4 (6)	14.1 ± 5.6 (6)	2.7 ± 2.0 (6)
June 1977 (control)	46.4 ± 9.8 (9)	45.4 ± 8.3 (9)	8.2 ± 3.2 (9)
October 1977 (sprayed)	93.7 ± 1.7 (6)	5.9 ± 1.8 (6)	0.4 ± 0.3 (6)
October 1977 (control)	94.6 ± 2.6 (5)	3.1 ± 1.6 (5)	2.3 ± 1.8 (5)

Trachelipus rathkei (Brandt): field populations:

In 1977 through 1979, data on T. rathkei were obtained by field sampling, and substantiated by laboratory observations on growth, reproductive biology, and pesticide susceptibility. For data pertaining to 1977-78, and the population model derived from them, the reader may be referred to Chapters VIII-X. Results from the 1979 season will be discussed in the following section.

The 1979 (diazinon) spray program was not successful due to technical inadequacies, which resulted in unknown, but certainly low rates of diazinon being applied in the orchard. The first spray event took place in early July, which is also unusually late in the season.

Isopods were collected from cryptozoan boards, as in previous years. A brief history of the plots sampled in 1979 is given here: Plot 8: used as control in 1977 through 1979. Plot 7: was used as second control plot in 1977-78; sprayed with diazinon in 1979. Plot 3: had received Guthion for three years (1976-78), was sprayed with diazinon in 1979.

A minimum of 12 boards (usually 20) were sampled per plot and date. Fig. V-1 shows mean numbers of T. rathkei found per board in the three plots. The catches were divided into two weight classes: $\leq$ 12 mg and > 12 mg.

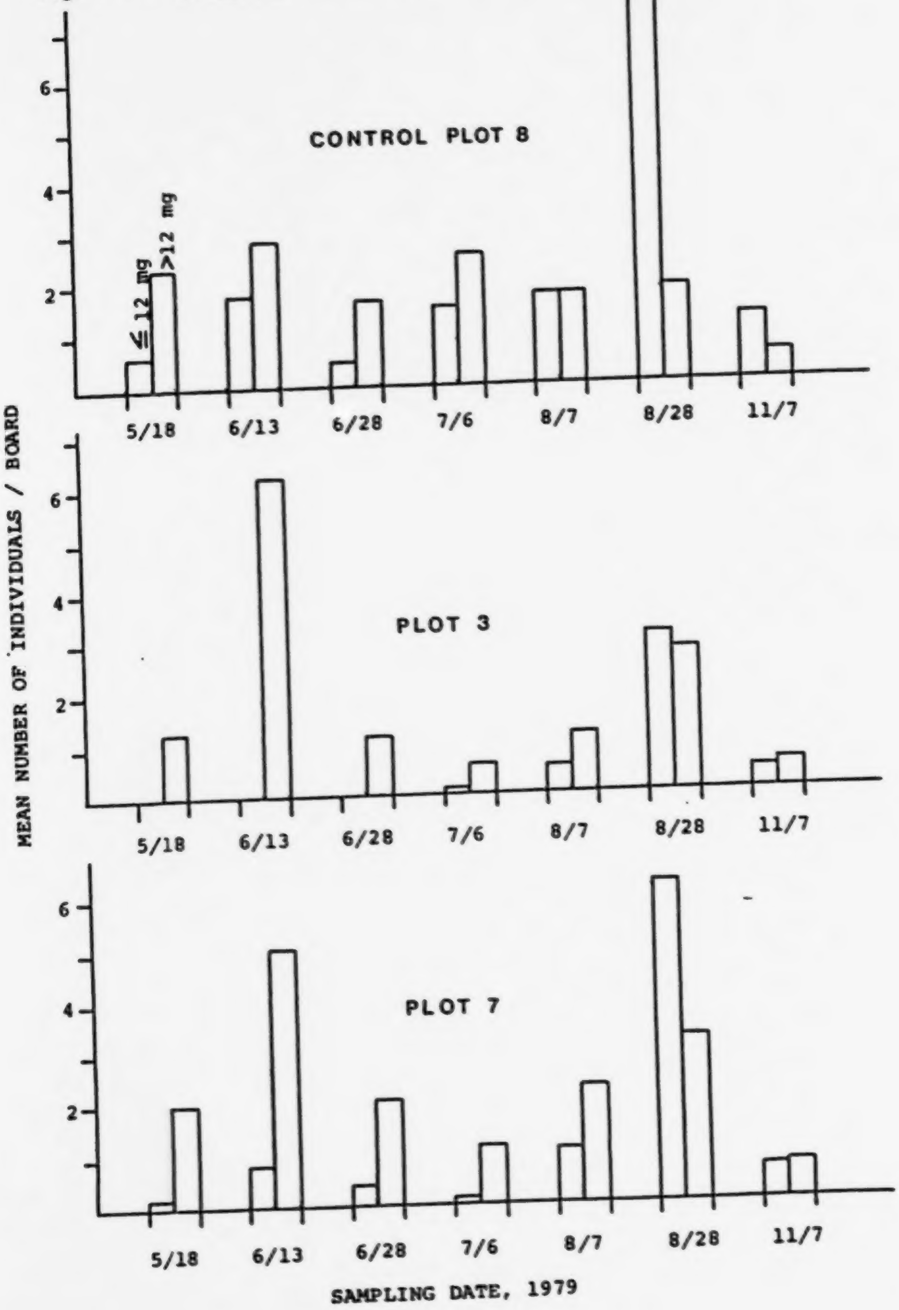
In plot 8 (control), the isopod population behaved much as in previous years. The conspicuous peak of small animals in August was due to the cumulative effect of two brood releases, which typically take place in late June and late July to August (Snider and Shaddy, 1980).

Plot 3, in May and June, showed the characteristic depletion of small animals which can be attributed to Guthion application (see Chapter X). The relatively large number collected in mid-June is likely to be due to immigration: in three consecutive years of pit-trapping (where any catches are solely the result of active animal movement), spring and fall samples were the only ones that yielded isopods in significant numbers. From July on, the population in plot 3 actually underwent a recovery. In August, the season's recruits were plainly evident. Their presence can be ascribed to three factors: a) the first brood release had taken place prior to diazinon application, and the young had time to grow just beyond the most vulnerable stages; b) diazinon, in laboratory experiments, was not as toxic to small animals as Guthion (at temperatures up to 21°C); and c) in all likelihood, much less diazinon reached the orchard floor than intended, so that even those young stemming from the second brood release may not have been affected by the pesticide at all.

Plot 7, except for the relatively low numbers captured in early July, showed strong similarities to the control plot. In fact, population structure indicated that diazinon application was ineffective: rather than being curtailed, recruitment was similar to that observed in the control plot in 1979, as well as to that found in plot 7 itself in 1977 and 1978, when it was used as control.

Although T. rathkei populations had been affected by Guthion application in previous years, one must conclude that under a subsequent light spray regime (or none at all) the populations would recover rapidly. Even if no immigration were taking place, it is likely that normal population levels would be attained within no more than two years.

Figure V-1. T. rathkei sampled in 1979 in three orchard plots.



CHAPTER VI

LABORATORY TOXICITY STUDIES ON SELECTED SOIL/LITTER INVERTEBRATES

INTRODUCTION

A number of invertebrates were tested for Guthion susceptibility in a series of preliminary screening experiments. Some species were chosen because they were available in mass cultures, and their biology was known, while others were selected because they occurred in the orchard and were potential candidates for organism models.

Resulting preliminary data, as well as the first season's sampling experience in the field, provided direction for further testing. Some taxa (chilopods, diplopods and oribatid mites, for instance) were difficult to track in the field, as well as being tolerant of Guthion. Others (i.e. lycosid spiders) could be neither collected nor reared in numbers large enough for testing, given the time and resources available. Thus laboratory experiments were later reduced to a few species. Selected data on Collembola, chilopods and isopods are summarized here. Data concerning *Trachelipus rathkei*, the species tested most extensively, are given in detail in Chapter X.

Materials and Methods:

Soil contamination with Guthion and diazinon:

Procedural details for Guthion contamination may be found in Chapter X. The same methods were used to make up diazinon-contaminated soil for contact toxicity observations on *T. rathkei*.

Contamination of yeast with guthion:

A slurry of powdered yeast, Guthion (50% W. P.) and acetone was stirred continuously until all acetone had evaporated, to yield yeast mixtures containing 1000, 2000 and 3000 ppm. By serial dilution of a 1000 ppm stock mixture with pure yeast, lower concentrations were obtained. Control yeast was prepared with acetone alone. All mixtures were kept frozen at -20°C, and small portions were removed from these frozen batches when needed. When feeding experimental cultures, yeast was placed in the center of a hardened plaster-charcoal substrate, in cylindrical plastic jars with tight lids, and was replaced daily throughout a given observation series.

Field-collected litter:

On four dates in 1978, surface litter was raked up in one Guthion-sprayed and one control plot and chopped, mixed, and brought up to 200% moisture in the laboratory. It then served as substrate for various invertebrates, particularly *T. rathkei*. For further details, refer to Chapter X.

Results

Collembola:

Adults of *Folsomia candida* (Willem) were exposed to Guthion by all three methods described above. *Hypogastrura armata* (Nicolet) was used in soil contact and oral toxicity experiments only.

F. candida (10 individuals in each of 10 replicate jars) were incubated at 21°C using field litter as the substrate, and total mortality after 6 days was recorded. As shown in Table VI-1, the animals incurred 92% mortality after 6 days exposure to litter collected 2 days after a spray event. A full month after the last spray period, field-collected litter was still toxic to F. candida. Judging by our soil toxicity data, showing that higher moisture content produces higher mortality, litter at less than 200% moisture might be less toxic to the species (except for rainy periods, litter in the field would not be that moist).

Table VI-1. Percent mortality of Folsomia candida after 6 days exposure to field-collected, Guthion-contaminated litter at 21°C. Replication: 10 individuals per each of 10 replicate containers.

		% mortality in:	
ppm residue (GLC analysis)	days since last spray	control litter	Guthion litter
25.7	2	4.0	92.0
3.1	30	7.0	15.0

In contrast to litter observations, contact (soil at 10% and 25% moisture) and oral (yeast) toxicity were assessed by means of 24-hour mortality records over 7 days. These tests were run at 15.5°C, with a total of 200 individuals of each species per run.

In both H. armata and F. candida. contact toxicity was more pronounced than oral toxicity (Table VI-2). At 10 and 100 ppm, moist soil was distinctly more toxic than dry soil. Soil at 1 ppm had no effect on either species, but at 10% moisture egg-laying was inhibited due to the marginal humidity regime. At 25% moisture both species produced viable eggs.

Table VI-2. Percent mortality of Collembola after 7 days exposure to Guthion in yeast and in soil at two moisture regimes, at 15.5°C. Replication: 40 individuals of each species in each of 5 replicate containers per dosage.

ppm Guthion			F. candida	H. armata
	CON	yeast	0.0*	0.3*
		soil, 10%	0.0	0.0
		soil, 25%	0.0	1.0
	1.0	soil, 10%	0.0	0.0
		soil, 25%	0.0	0.0
	10.0	yeast	0.5*	1.0
		soil, 10%	5.0	2.0
		soil, 25%	26.0	29.0
	10.0	yeast	5.0*	9.5
		soil, 10%	20.0	28.0
		soil, 25%	39.0	40.0
		yeast, 1000 ppm	38.5*	16.0
		yeast, 2000 ppm	55.0	15.0
		yeast, 3000 ppm	51.8	23.0

*) Averaged results of 2 replicate runs under identical conditions.

At termination of the contact toxicity tests (25% moisture) half of the surviving animals were transferred to control soil for a 4-day recovery period. In the 1 ppm sample, viable eggs were again produced. The 10 and 100 ppm series, animals which had begun to show slightly uncoordinated movement continued to die. None showed signs of recovery.

In oral toxicity tests, we noted that only yeast with low pesticide concentration was readily eaten. But apparently even the small amount of food initially ingested by *F. candida* produced 55% mortality at 2000 ppm, and 51.8% at 3000 ppm (Table VI-2); of *H. armata*, 9.5% died at 100 ppm, compared to 3% of *F. candida*. At 3000 ppm, the relatively low mortality of *H. armata* (23%) probably indicates that the food was avoided.

Tomlin (1975), using 17 insecticides other than Guthion, showed that *H. armata* was much more tolerant than *F. candida* to almost all compounds tested. In the present study, however, the two species behaved very similarly when kept on soil at 10 and 100 ppm (Table VI-2). Tomlin's conclusions on interspecific susceptibility differences were based on 24-hr mortalities. For comparison, Table VI-3 shows 24-hr Guthion mortality records. Using soil, neither 24-hr nor 7-day mortalities (Table VI-2) showed appreciable interspecific differences. Using yeast as the pesticide vehicle, *F. candida* did incur higher mortality after 24 hours, but only levels of ≥ 1000 ppm supported Tomlin's (1975) conclusions concerning the two species.

Folsomia candida has been used in pesticide screening studies by other workers (Thompson, 1973; Scopes and Lichtenstein, 1967) and has been subjected to Guthion by Thompson and Gore (1972). The latter authors found that mortality after 24 hours amounted to 70% at 24°C, and 20% at 13°C; the substrate was Plainfield sand at 1 ppm Guthion. The same substrate with 10 ppm Guthion resulted in 100% mortality within 24 hours, at both temperatures. In sharp contrast, we recorded zero mortality at 1 ppm, at 15.5°C, and the production of viable eggs testified to the health of the animals. Even after 7 days on 10 ppm soil (at 25% moisture), mortality in *F. candida* was only 26% (Table VI-2), and 24 hours exposure had no effect at all (Table VI-3).

Table VI-3. Percent mortality of Collembola after 24 hours exposure to Guthion in soil (25% moisture) and in yeast, at 15.5°C. Replication: 200 animals of each species per dosage.

	ppm in soil				ppm in yeast					
	CON	1	10	100	CON	10	100	1000	2000	3000
F. candida	0.0	0.0	0.0	1.0	0.0	0.0	0.3	8.3	6.2	8.1
H. armata	0.0	0.0	0.0	1.0	0.0	0.5	0.0	0.0	0.0	0.0

Determination of what constitutes "death" may have some bearing on these discrepancies. Thompson and Gore (1972) counted animals as dead when they were unable to actively run or spring, while we waited until almost total inactivity except for slight twitching of appendages). However, inability to run after 24 hours would surely have led to total immobility within 7 days or less: the discrepancy between 100% and 26% mortality remains.

Differences in soil type, pesticide formulation or solvents could furnish more valid considerations in a comparison with Thompson and Gore's (1972) results. Although this has not been documented for Guthion, Harris

(1967) did show the importance of soil type in toxicity studies: LD$_{50}$'s for crickets kept on fine sandy loam increased by factors of 8.3 (for diazinon) and 9.4 (for parathion) compared to crickets on a clay soil high in organic matter (Thompson and Gore, 1972), so that pesticide activity would likely be much higher than in our soil which contained > 20% clay and ≥ 3% organic matter.

Of equal importance, and equally dependent on soil type, is the effect of the substrate's water content. Harris (1970) documented that the bioactivity of certain insecticides in sandy loam increased by a factor of up to 100x with increasing moisture content. These effects were greatest in light mineral soils, but were negligible or even reversed in muck soils (Harris, 1967). In Brookston clay loam (somewhat similar to our orchard soil although higher in organic matter), moisture effects were intermediate (Harris, 1967).

In our experiments, Guthion at 10 ppm was also less active at the lower soil moisture (Table VI-2): by a factor of 5.2 for *F. candida*, and 14.5 for *H. armata*. At 100 ppm, the moisture effect was less pronounced (a factor of < 2.0 for both species).

Chilopoda and Diplopoda:

The centipede *Tidabius tivius* (Lithobiidae) was tested on orchard soil containing from 3 to 100 ppm Guthion. Table VI-4 summarizes cumulative 7-day mortalities. As expected, first instars proved to be more susceptible than adults. Decreasing susceptibility with increasing body size also became clear in isopods (Chapter X), as well as in oral toxicity tests with the diplopod *Polydesmus inconstans*: yeast at 10 and 100 ppm Guthion doubled the mortality of instars I over that of adults. However, neither stage was very susceptible to Guthion: a dosage of 1000 ppm was needed to produce appreciable effects (≥ 40% mortality) in both stages.

Table VI-4. Percent mortality of *Tidabius tivius* (Chilopoda) after 7 days on Guthion-contaminated soil (25% moisture) at 26.7°C. Replication: 20 individuals per stage and concentration.

	ppm Guthion in soil						
	CON	3.0	5.0	10.0	25.0	50.0	100.0
Instar I	0.0	5.0	20.0	25.0	100*	100**	-
Adults	0.0	-	0.0	0.0	0.0	100	100**

*) 100% in 48 hours
**) 100% in 24 hours

Both *T. tivius* and *P. inconstans* occurred in the orchard, and were at one time considered as candidates for modeling. The diplopod population was extremely sparse, however, and could not be sampled by either pit-trapping or by the cryptozoan board technique. And, while adults of *T. tivius* were relatively numerous under cryptozoan boards, immature stages of the species could not be sampled accurately by any means. For these reasons, laboratory observations on these species were later discontinued.

Isopoda:

Initially, both Trachelipus rathkei and Armadillidium nasutum were used in toxicity experiments. Once it became clear that only the former species occurred in the orchard, tests were restricted to T. rathkei, and pertinent data are reported in Chapter X.

The few test runs performed with A. nasutum are summarized in Table VI-5, and contrasted to data from a concurrent test of T. rathkei. Somewhat lower mortality of A. nasutum on soil at 10 ppm may have been due to the fact that this species tends to be larger and bulkier: in subsequent tests of T. rathkei, an inverse relation between weight and susceptibility to Guthion was documented (Chapter X).

Table VI-5. Toxicity of Guthion to adult isopods at 15.5°C (soil: 25% moisture), as percent mortality after 7 days exposure.

	ppm in yeast				ppm in soil			
	CON	10	100	1000	CON	1	10	100
A. nasutum	0.0	5.0	0.0*	100	5.0	5.0	5.0	100
T. rathkei	-	-	-	-	0.0	5.0	15.0	90

*) All animals severely affected (inactive, body lesions evident).

In A. nasutum, some avoidance of contaminated yeast was observed, but ingestions of yeast with 100 ppm Guthion affected the animals severely, though slowly; after 7 days exposure, all were inactive, rolled up, and showed lesions with leaking body fluids, indicating imminent death (Table VI-5).

Because reduced feeding rates were observed in oral toxicity tests, the possible ability of isopods to detect and avoid contaminated substrates was investigated. Chopped litter at 200% moisture was distributed in plastic dishes such that quadrants of contaminated and control litter alternated. Dosages were 0.5, 5.0 and 10.0 ppm; control dishes contained 4 quadrants of uncontaminated litter. The covered dishes were kept in the dark at 15.5°C after two adult isopods had been introduced into each of 5 replicate dishes per dosage and species (both T. rathkei and A. nasutum were tested). Three times daily, for 5 consecutive days, the containers were taken out a few at a time, and an immediate count was made of the position of the animals with respect to the four quadrants. Moving versus immobile (resting) numbers were recorded.

Analysis of variance comparing the numbers of animals found in each quadrant was performed, both with inclusion and exclusion of moving individuals. None of the results were significant, indicating that contamination of the litter did not influence the animals' choice of resting places. Active avoidance of contaminated strata of the orchard floor was thus made highly unlikely, and chances of isopods encountering contaminated substrates in the field probably depend solely on movement of the animals in response to microclimatic conditions.

Table VI-6. Replication in diazinon toxicity experiments with T. rathkei: numbers of animals observed per weight bin and ppm diazinon, at 26.7°C.

Wt bins: upper limit, mg	ppm diazinon in soil					
	CON	1.0	3.0	5.0	10.0	20.0
0.69	-	1	-	-	-	-
0.97	2	1	-	-	-	-
1.34	3	-	1	-	-	-
1.86	-	2	4	2	1	-
2.59	6	8	3	5	3	-
3.60	4	10	10	15	2	-
5.00	10	19	18	22	5	-
6.22	12	13	14	13	4	-
7.25	4	9	3	8	1	-
9.64	4	4	6	6	5	-
12.00	2	2	2	2	3	-
15.09	2	-	5	7	5	-
18.97	7	-	7	7	9	2
23.86	13	-	10	25	12	6
30.00	19	-	12	25	21	6
31.75	5	-	2	5	6	1
33.60	8	-	4	5	5	3
35.57	5	-	2	6	3	2
37.65	6	-	5	7	8	2
39.84	4	-	5	3	3	1
42.17	3	-	2	4	8	3
44.63	2	-	-	1	12	2
47.24	2	-	-	-	5	1
50.00	1	-	-	-	5	1
53.03	1	-	-	-	8	-
56.23	1	-	-	-	3	2
59.64	-	-	-	-	3	1
63.25	-	-	-	-	3	-
67.07	-	-	-	-	-	1
71.13	-	-	-	-	2	2
75.44	-	-	-	-	1	-
80.00	-	-	-	-	-	-

For instars II, a separate series was observed at selected levels of diazinon (see summary of results in Table VI-11).

For these tests, we used soil from a single large block, taken in an orchard control plot, sieved, dried, and mixed in large vats before diazinon-contamination of weighed subsamples. In spite of repeated, careful efforts to contaminate soil evenly, the substrates finally used all contained somewhat less than the desired concentrations. (Examples of GLC extraction results of contaminated subsamples are given in Table VI-7).

Trachelipus rathkei: diazinon toxicity:

In anticipation of sampling results from the last spray season (diazinon application) a pilot contact experiment was set up using T. rathkei, orchard soil contaminated with diazinon in the laboratory, and constant termperatures of 15.5, 21 and 26.7°C. Experimental procedures were essentially identical to previous Guthion tests (see Chapter X), except for the way in which test animals were selected and pooled.

Instars II and small individuals up to about 1 mg in weight were obtained from reproducing laboratory cultures. All other animals were collected from campus woodlots and incubated at the three temperatures for at least one week. They were then weighed individually, assigned to weight bins according to those specified in the T. rathkei model, and used for tests.

A diazinon "run" at a given dosage and temperature (unlike Guthion runs) therefore consisted of varying numbers within each weight bin, distributed such that the most efficient use would be made of the > 2000 animals weighed at the time. Table VI-6 provides an example of how animals were assigned to bins in the test series incubated at 26.7°C; similar distributions were set up at the lower temperatures. The distinctly uneven distribution of replicate individuals over the entire weight range is a direct reflection of the weight distribution in the isopod population at the time of collection (August - September).

Table VI-7. Results of GLC analyses of diazinon-contaminated soil (adjusted for GLC extraction efficiency) prior to using the soils for toxicity experiments with T. rathkei.

Desired ppm	Detected ppm mean ± S.E.	n Samples	range ppm
3.0	2.81 ± 0.09	3	2.60-2.95
10.0	9.02 ± 0.59	3	8.21-10.45
20.0	17.97 ± 1.58	3	15.20-21.70

Table VI-8 shows mortality percentages for those weight classes (bins combined) which contained more than five individuals, after discarding approximately 15% of the data because the animals had molted during the observation period. Both 7-day and 10-day mortalities are given. In most cases, and irrespective of temperature and pesticide concentration (except at 20 ppm) mortality did not increase from the 7th to the 10th day.

Table VI-8. Percent mortality of *T. rathkei* exposed to diazinon-contaminated soil at three temperatures. Values not in parentheses are cumulative 7-day mortalities; values in parentheses are 10-day mortalities (same animals, 3 days later). Weight bins as specified in Table VI-6 were combined into larger weight classes, to obtain a minimum of 5 replicate animals per class.

Weight class, mg	T°C	Control	DIAZINON, PPM			
			3.0	5.0	10.0	20.0
1.35-5.00	a*	4.0(4.0)	0.0(6.3)	8.3(16.7)	- -	100(100)
	b*	0.0(7.7)	13.5(13.5)	- -	- -	- -
	c*	0.0(0.0)	42.9(54.3)	47.7(59.1)	90.9(90.9)	- -
5.01-12.00	a	4.2(4.2)	0.0(3.4)	30.8(30.8)	- -	- -
	b	0.0(1.1)	3.7(7.4)	- -	- -	- -
	c	0.0(4.5)	20.0(28.0)	55.2(69.0)	100(100)	- -
12.01-30.00	a	2.8(2.8)	0.0(12.5)	4.5(4.5)	19.0(19.0)	18.2(51.5)
	b	0.0(0.0)	3.6(3.6)	0.0(0.0)	15.4(30.8)	66.1(81.4)
	c	12.2(12.2)	17.6(20.6)	17.2(29.7)	72.3(76.6)	100(100)
30.01-39.84	a	8.3(8.3)	- -	0.0(0.0)	0.0(0.0)	25.0(60.0)
	b	0.0(0.0)	0.0(0.0)	0.0(5.3)	8.3(3.3)	64.9(78.4)
	c	3.6(7.1)	11.1(18.8)	3.8(11.5)	51.9(60.0)	100(100)
39.85-50.00	a	0.0(0.0)	- -	0.0(0.0)	12.5(12.5)	36.4(55.6)
	b	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	97.6(97.6)
	c	12.5(12.5)	- -	20.0(20.0)	53.3(60.0)	100(100)
50.01-63.26	a	0.0(0.0)	- -	- -	- -	- -
	b	- -	- -	- -	- -	84.6(84.6)
	c	- -	- -	- -	52.9(64.7)	100(100)

---

*) Temperatures: a = 15.5°C; b= 21.1°C; c = 26.7°C; all ± 1°C.

Like Guthion (Chapter X) and other insecticides (Harris 1971), biological activity of diazinon increased with increasing temperature, but magnification factors were consistent neither within weight class nor within dosage (Table VI-8).

Using *F. candida* as test species, Thompson and Gore (1972) found diazinon to be more toxic than Guthion in a Plainfield sand substrate. Since that comparison was of interest in the present study as well, our preliminary diazinon data were summarized such that they could be contrasted to Guthion data. Where ≥ 10 animals had been observed in selected weight classes (2-3, 5, 15-20, 30-40, and approximately 50 mg), diazinon and Guthion toxicities could be opposed (Table VI-9).

Table VI-9. 7-day mortality percentages (corrected for control) for T. rathkei reared on Guthion- and diazinon-contaminated soil. Data included only if a minimum of 10 replicate test animals had been observed per weight class and dosage.

	Dosage level								
	3.0		5.0		10.0		20.0		
Animal Weight, mg	GUTH	DIAZ	GUTH	DIAZ	GUTH	DIAZ	GUTH	DIAZ	
2-3	32.9	0.0							
15-20			26.3	6.8	31.6	16.7			15.6°C
30-40					15.0	0.0	26.7	23.6	
2-3	70.3	15.4							
15-20			10.0	0.0	32.5	16.7			
30-40			5.0	0.0	5.0	8.3	100.0	64.9	21.1°C
50							5.0	83.3	
2-3	38.9	46.2	55.6	60.0					
5	0.0	28.6	60.0	46.2	90.0	88.9	90.0	88.9	
15-20					55.0	68.3	55.0	68.3	26.7°C
30-40			20.0	0.0	7.2	55.4	67.8	100.0	
50					0.0	84.6			

The number of comparisons thus obtained are limited, and require substantiation with large numbers of equal-weight individuals. However, presented simply in qualitative terms (Table VI-10), diazinon appeared to behave in a way unexpectedly different from Guthion. At lower temperatures, Guthion was more toxic than diazinon at 3, 5 and 10 ppm, to animals of all sizes including II instars (Table VI-11). At 20 ppm, 21°C, large T. rathkei were more susceptible to diazinon. At 26.7°C (with 2 exceptions at 5 ppm) diazinon was more toxic than Guthi[illegible]articularly to the larger-sized animals. These limited data indicate tha[illegible]he distinct inverse relationship between body size and pesticide susceptibility (Chapter X) as documented for Guthion, may not hold true for diazinon; or may hold true only under certain conditions (possibly combined functions of dosage and temperature)

Table VI-10. Relative toxicity of Guthion and diazinon to *Trachelipus rathkei* at three temperatures. For details see Table VI-8 and Chapter X.

	Temperature, °C		
	15.6	21.1	26.7
3.0	guth > diaz	guth > diaz	diaz > guth
5.0	guth > diaz	guth > diaz	diaz > guth (for 2-3 mg)
10.0	guth > diaz	guth > diaz	diaz > guth (for lower weights) diaz >> guth (for high weights)
20.0	guth ≈ diaz	guth > diaz (for 30-40 mg) diaz >> guth (for 50 mg)	diaz > guth

Table VI-11. Toxicity of diazinon-contaminated soils to II. instar *Trachelipus rathkei* at 15.6°C, contrasted to Guthion toxicity at the same temperature. All data corrected for control by Abbott's formula. Replication: minimum of 40 animals per run, (two per replicate container).

	Dosage, ppm		
	1.0	3.0	20.0
diazinon 7-day, %	10.2	34.3	100.0
diazinon, 10-day, %	16.3	34.3	100.0
Guthion, 7-day,%	29.9	55.8	100.0

CHAPTER VII

DESCRIPTIONS OF SPIDER, EARTHWORM, AND SPRINGTAIL MODELS

SPIDER MODEL DESCRIPTION

The spider model simulates the population dynamics of a temperate-climate spider with a two-year life cycle, such as the wolf spider (Lycosidae). The spider is assumed to grow during its first two summers and breed during its third. Most female Lycosids produce a brood in early summer, followed by a second brood later in the year (Edgar, 1970, Eason and Whitcomb, 1965). The Lycosidae pass through a number of distinct instars separated by molts. Since most of the demographic data for parameterizing the model are from Edgar's work with *Lycosa lugubris*, we have separated the spider population into eight instars, which Edgar found to be a typical number of instars for *Lycosa lugubris*, plus adults. The model tracks only female spiders.

The passage of spiders through an individual instar is modeled as a distributed delay process (see Manetsch, 1976). The delay parameter for each instar is determined each day by dividing the degree-day threshold for the instar (the number of degree-days necessary for completion of the instar) by the degree-days accumulated on that day, which yields the mean number of days the spiders should spend in the instar at the current temperature.

Individuals are removed from the population at each time step to simulate "natural" mortality, cannibalism, and pesticide-induced mortality. Values for "natural" mortality rates were taken from Edgar (1971), while values for cannibalism mortality rates were approximated to keep the population size close to observed field values since no data exist concerning cannibalism rates. It was assumed that spiders of a given instar would be consumed only by spiders of the same instar (at rates proportional to the number of spiders in the instar) and spiders of larger instars (at rates proportional to the product of the number of larger spiders and the number of spiders of the given instar).

For pesticide-induced mortality, a model similar in form to the one used in the *Trachelipus* model (described in Chapter X) was used. The cumulative mortality expected at the end of seven days' exposure to the present day's pesticide concentration is calculated from a regression of mortality vs. pesticide concentration for first instar spiderlings and corrected for temperature and size differences. As in the *Trachelipus* model, the probit of the current day's mortality thus calculated is weighted and averaged with the cumulative mortality experienced in the previous time-step to yield a new expected cumulative mortality. As in the *Trachelipus* model, corrections are made for graduations into and out of an instar.

According to Edgar (1971), spiders hatched in a given year reach, at most, the fifth instar by winter. Likewise, these spiders do not develop past the eighth instar (subadult) during the following year. The model simulates this behavior by storing any spiders which graduate from the fifth and eighth instars from late summer onward and then releasing them after winter into the sixth instar and adult, respectively.

Another developmental phenomenon to be modeled is the rapid growth of individuals from the second brood. To simulate the increased growth, the degree-day thresholds for the spiders in the first and second instars are reduced during the late summer. This treatment is justified since eggs from the second brood are larger than those from the first (Edgar, 1971) and would be expected to develop more rapidly.

All adults breed for the first time after accumulating a sufficient number of degree-days. All adults produce the same number of eggs, but 10% of the eggs are subtracted as losses to parasitism. After a second degree-day breeding theshold is passed, 35% of the adults breed for a second time. Again, all breeding adults produce the same number of eggs, but the second brood is smaller than the first.

Since the spiders diapause during the winter, the model is turned off late in the fall and is turned back on in spring after a degree-day threshold is reached.

Since the model tracks only female spiders, the population size predicted by the model must be doubled to yield the "true" population size, except for the adult population from June onward since adult males die in June while the females live until October (Edgar, 1971).

EARTHWORM MODEL DESCRIPTION

The earthworm model simulates population dynamics of the lumbricid earthworm Allolobophora caliginosa. This earthworm commonly resides in the upper ten centimeters of soil, although it may venture deeper than 30 centimeters when conditions become unfavorable (e.g., too cold or hot, or too dry). Its life expectancy is normally less than two years, and growth is hermaphroditic; all adults are included in the reproductive process. The model tracks the number of cocoons developing and the biomass of the juvenile and adult populations.

The development of the cocoons produced by the adults is temperature dependent, and juveniles hatch from the cocoons after a degree-day theshold is passed. Cocoon mortality is assumed to be zero since cocoons are apparently very resistant to temperature and moisture changes.

New hatchlings are added to the juvenile population after converting their population from numbers to biomass. The juveniles gain weight at a rate which diminishes as they grow, in accordance with the observations of Murchie (1960). The growth rate is adjusted downward during any time-step if soil moisture or temperature are outside the ranges found to be optimal for growth. In addition, the growth rate is decreased as the population biomass density increases, utilizing a carrying-capacity term which multiplies the growth rate by a factor ranging linearly from unity (when the biomass is zero) to zero (when the carrying capacity is exceeded). To simulate mortality, biomass is removed each time step at a rate which increases exponentially with decreasing soil moisture and exponentially with temperatures outside the optimal growth range. Other sources of mortality have been found to be insignificant (Van Rhee, 1961).

After juveniles have matured for 55 weeks, they are added to the adult population. The biomass of the adult population is increased each time-step at a rate equal to the maximum growth rate (taken from the data of Barley (1959), Satchell (1967), and Waters (1955)) scaled by factors for temperature and soil moisture, and the carrying-capacity term used to express biomasss density limitation as in the case of the juvenile growth rate.

The mortality rate used is the same used for the juvenile population.

Since it was assumed that the reproduction rate is proportional to adult biomass, the number of cocoons produced during any time-step is determined by multiplying the adult biomass by the cocoon production rate. The cocoon production rate, in turn, is determined by multiplying the maximum production rate (taken from Evans and Guild, 1948) by factors which scale the production rate for moisture, temperature and crowding effects. It should be mentioned that the scaling factor for moisture effects used here is the same one used throughout the model whenever corrections must be made for moisture conditions. The function used to determine the scaling factor was generated from the data of Evans and Guild (1948). Their data were also used to generate the temperature scaling factor for cocoon production. However, the scaling factor used to adjust the growth rate of juveniles and adults for temperature effects was derived from a function fabricated to yield an increasing growth rate with increasing temperature which levels off at a constant value of unity for temperatures above 20°C.

FOLSOMIA MODEL DESCRIPTION

The *Folsomia* model simulates the population dynamics of a hypothetical springtail of the family Isotomidae, which will hereafter be referred to only by the generic name *Folsomia*. Almost all the data used stem from a study of *Folsomia quadrioculata* by Gregoire-Wibo (1975), but pesticide-induced mortality rates are those recorded for *Folsomia candida* in our laboratory. *Folsomia* has a life span of nine months, but three separate, overlapping generations exist during the year. That the life expectancies of the three generations are not the same. Individuals of each generation pass through three life stages: prejuvenile (which covers the egg stage up to hatching), juvenile, and adult (which begins when an individual begins egg-laying). *Folsomia* reproduce parthenogenetically, so all individuals are tracked by the model.

The progression of individuals through the life stages is simulated as a distributed delay process, as in the other organism models. The rate of advancement is based on the growth rate, which is determined from a degree-day model of growth. The variability in the durations of the corresponding life stages for the three generations is a reflection of the influence of temperature on the growth rate.

Adults produce eggs continuously in the model at a rate proportional to the growth rate, and lay eggs at a faster rate in the warmer months than in the cooler months. In addition, the total number of eggs laid by adults in the warmer months is greater than the egg production of adults living in the cooler months.

Sources of mortality considered by the model include predation, other "natural" mortality and pesticide-induced mortality. Natural mortality rates were taken from the data of Gregoire-Wibo (1975), while the predation rates were fabricated to keep the population from growing without bound. Pesticide-induced mortality rates are determined from a linear regression of probit mortality vs. log concentration established in the lab. The raw mortality rate (in probits) obtained from this regression is treated as in the *Trachelipus* model (including correction for graduations) to yield a more accurate estimate of the expected mortality.

CHAPTER VIII

THE ECOBIOLOGY OF TRACHELIPUS RATHKEI

After extensive investigation in both laboratory and field, McQueen (1976c) was able to construct a successful demographic model for a population of Trachelipus (Tracheoniscus) rathkei (Brandt 1833) in Ontario, Canada. The work presented here was undertaken in a similar effort to model a Trachelipus population, and the information given by McQueen provided useful reference points. While McQueen's sampling site was a gravel-covered field, the present study was carried out in an orchard in mid-Michigan; it formed part of a project concerned with assessing the fate and effects of azinphosmethyl spray application. Preliminary results pertaining to the effects of the pesticide on Trachelipus have been published by Snider (1979) and are given in Chapter IX. The data stemming from unsprayed control plots form the basis of this report. Together with some of the laboratory results given here, they have led to the construction of a model of the Trachelipus population in the orchard (see Chapter X). In accordance with the structure of that model, the bulk of the data we discuss concerns only the females of the species.

MATERIAL AND METHODS

In 1976, experimental plots were established near Grand Rapids, Michigan, in an apple orchard which had been left untended for 20 years. The two control plots in use during 1978 contained a total of 24 boards, 35 x 15 cm and 2 cm thick. Half of them were placed on the ground underneath tree canopies, the others out in the unshaded alleys between trees. Isopods were collected periodically from the underside of the boards as well as from the surface-soil and litter beneath them. They were taken in the laboratory, measured, sexed, checked for breeding condition, and returned to the boards they came from.

Field-collected animals were not weighed; instead, multiple regressions--using head width and width of the seventh thoracic segment--were run to develop equations that would give the best estimates of weight. For animals with a head width exceeding 1.0 mm, the regression equation:

$$Wt = 3.514a^3 + 0.454b^3 - 1.617,$$

where a = head width and b = thoracic width, gave an r^2 of 97%. For animals with a head width < 1.0 mm, a second equation had to be developed:

$$Wt = 1.501a^3 + 0.578b^3 - 0.167,$$

with a r^2 of 94%. For first and second instars, which lack a seventh segment, mean weights were obtained in the laboratory and used for field-caught individuals: 0.5 ± 0.05 mg (n = 15), and 0.7 ± 0.13 mg (n = 15) respectively.

When validated against size and weight gain of 65 individuals, observed through at least 2 consecutive molts, both equations predicted a "mid-instar weight"; i.e., the values fell between the low weights immediately after a molt and the maximum weight obtained prior to the next molt.

Assignment of field-caught females to weight-related developmental classes is likely to be more accurate if estimated rather than actual weights are used: females carrying brood gain a large amount of weight, but return to their true size-related weight after release of the progeny.

For laboratory observations, Trachelipus were collected at various times of the year, beginning in early April, in woodlots around MSU campus as well as in the Grand Rapids orchard site. Depending on the use for which they were intended, females were kept in isolation, temporarily paired with males, or held in communal stock cultures. Isolates and pairs were kept in cylindrical plastic jars with snapon lids (35 mm diameter by 25 mm high); stocks were reared in larger plastic containers.

The substrate consisted of a layer of plaster of Paris and charcoal, mixed with water, poured, set and remoistened; and above it a layer of duff, rotting wood and woodland soil. This material was replaced periodically to provide cover and food in addition to the powdered yeast used as staple diet. Distilled water was added when necessary to keep the substrate moist, but not wet. The cultures were kept at constant temperatures of 15.6, 21.0 and 26.7°C. Observations were made at intervals of 1 to 3 days.

Throughout this publication, reference will be made to weight classes. The Trachelipus model, (Chapter X) simulates growth as temperature-dependent advancement through these classes, which can be characterized as follows:

0.5-5.0 mg: following McQueen (1976c), this class is termed "prejuvenile." The sexes cannot be distinguished; where appropriate, total numbers of prejuveniles captured in the field were halved in the calculation of results (assuming a 1:1 sex ratio).

5.01-12.0 mg: juveniles; the sexes are dinstinguishable, but the females are not yet capable of reproducing.

12.01-30.0 mg: young adults; the lower limit of this class was defined according to field evidence of breeding potential (details given later on).

30.1-50.0 mg: adult females, which form the bulk of the breeding segment of the population at certain times of the season.

>50.0 mg: females nearing or in their second year of life; they never constituted a conspicuous segment of the population. Individuals exceeding 80 mg were rarely encountered in the field, but laboratory animals could be reared to weights beyond 100 mg. With respect to laboratory data, these females will therefore be classified as "50-80 mg class."

Preliminary feeding experiments were carried out to determine whether yeast would be an adequate food source for Trachelipus in culture. Yeast was compared to Purina Rabbit Chow which, since Merriam's (1971) determination of its superior nutritive value, has been used for isopod cultures by other authors (McQueen and Carnio 1974; McQueen 1976a,c). Newly hatched individuals were raised in isolation for 130 days at a constant temperature of 26.7°C. Males were discarded once the sexes could be distinguished.

Fig. VIII-1 shows mean weight gain of females on the two diets, summarized at 10-day intervals. Yeast out-performed Purina slightly, and was henceforth used as the main diet in all cultures, especially since it had a lesser tendency to mold during non-feeding periods of isopods (e.g. before a molt). Mortality was nil in the Purina-fed series, and was also nil in the yeast series after the first 21 days. Up until then, three of the initial thirty-six replicates had died, but their sex was not known at the time.

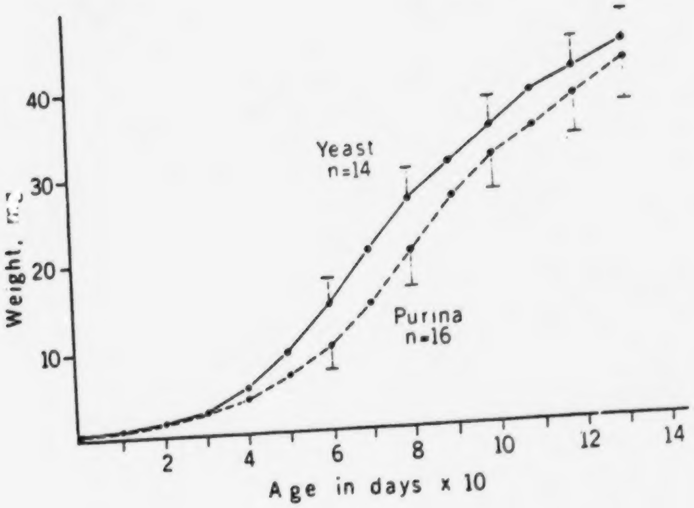


Figure VIII-1. Growth of *Trachelipus* females on two diets (mean weights at 10-day intervals, plus or minus one S.D. at selected ages).

RESULTS: LABORATORY

BREEDING PERIODICITY

As shown in Table VIII-1, the duration of gravidity is temperature-dependent, ranging from about 18 days at 26.7°C to 51 days at 15.6°C. The rest interval between brood release and the next brood molt is not as clearly influenced by temperature (Table VIII-2). The incidence of a sterile molt intervening between two brood molts was most common in females weighing less than 30 mg at the onset of breeding. It allowed them to undergo a brief period of growth, and they frequently reached weights of 30 mg or more before producing their second brood.

The production of two or three consecutive broods appears to be the rule in laboratory-grown individuals of other species of isopods (Verhoeff 1920, Bakker 1956, McQueen and Carnio 1974). For Trachelipus, McQueen (1976c) reported that 83% of mated adults produced one brood, and 42% a second, with some indication that the reproductive rate might be temperature-dependent.

The data in Table VIII-3 were classified by female weight prior to the first brood molt, in order to assess the reproductive capabilities of a given weight class. Roughly half of these females were mated in the laboratory, and their pre-breeding weights, ranging from 18 to 81 mg, were known. All of them produced eggs within a short period of time (i.e. 100% of these females, at all temperatures, had a first brood). The remainder of the observations in Table VIII-3 stems from individuals collected in the field in late May, already carrying their first brood of the season. For these, pre-brood weights could be estimated after assessing the size gain connected with the brood molt of 28 females in the 30-50 mg range (mean gain of 0.1 ± 0.02 mm in head width, and 0.2 ± 0.07 mm in thoracic width). After subtraction of these means from the measurements of the females, pre-breeding weights were estimated by regression equation.

At least at constant temperatures, the production of second broods appeared to be influenced by initial weight, since a larger percentage of the heavier females tended to breed twice at all temperatures. It also seemed temperature-dependent, since the incidence of second broods increased with increasing temperature. Third broods were common at 26.7°C, and only at that temperature; one female even produced four consecutive broods.

In long-term observations it was found that reproduction then ceased, but that the same pattern was repeated after varying lengths of time (Table VII-4). By then, females weighed about 50 mg or more, and again produced one to three broods. Since none of the animals were allowed to mate since their very first brood, observations by Heeley (1941) concerning the sperm storage capability of isopods were confirmed. However, sperm viability was affected by temperature: while at 15.6 and 21°C over 90% of all broods were successful, 89% of the females kept at 26.7°C prematurely ejected clusters of undeveloped eggs. The occurrence of third and fourth broods at 26.7°C is reminiscent of the pattern observed in the first breeding period, with its evidence of temperature-dependency.

Since all individuals had been field-collected in the spring, those with initial weights exceeding 50 mg had almost certainly reproduced the preceeding year. For these,the second breeding period observed in the laboratory actually represented a third, suggesting a reproductive potential that is continuous throughout the life span of Trachelipus. Its rhythmicity, determined in the field by seasonal temperature evolution, is retained to a certain degree at constant laboratory temperatures.

FECUNDITY

As has been reported by other authors (Paris and Pitelka, 1962, Brereton, 1956, McQueen and Carnio, 1974, McQueen, 1976c) the number of young produced by isopods is linearly related to size or weight of the female. In Trachelipus, it ranges from about 10 young for females less than 20 mg to over 30 young for those more than 50 mg in weight. The highest number produced in culture was 60 young, by each of two females weighing 70 and 90 mg.

TABLE VIII-1. DURATION OF GRAVIDITY, IN DAYS, OF Trachelipus FEMALES KEPT AT THREE TEMPERATURES.

T°C	N	Mean duration	S.D.	Range
15.6	28	51.4	±1.5	48-54
21.0	54	30.7	±1.3	28-35
26.7	87	17.6	±1.0	16-20

TABLE VIII-2. DURATION, IN DAYS, OF THE REST INTERVAL BETWEEN BROOD RELEASE AND THE NEXT BROOD MOLT OF Trachelipus.

T°C	N	Mean duration	S.D.	Range
15.6	20	16.9 ±	3.4	13-27
21.0	18	17.2 ±	4.3	8-25
26.7	50	13.4	±5.2	7-27

TABLE VIII-3. NUMBER OF CONSECUTIVE BROODS PRODUCED BY Trachelipus FEMALES IN THE FIRST BREEDING PERIOD (Percent *italics*).

T°C	Pre-brood weight (mg)	No. obs. (1st brood)	No. producing 2nd brood			
					3rd brood	
15.6	<30	12	2	*16.7*	0	
	30-50	25	11	*44.0*	0	
	>50	10	8	*80.0*	0	
21.0	<30	17	5	*29.4*	0	
	30-50	15	10	*66.7*	0	
	>50	18	14	*77.8*	0	
26.7	<30	17	17	*100*	2	*11.8*
	30-50	20	20	*100*	16	*80.0*
	>50	11	11	*100*	5	*45.5*

Note: Assignment to weight classes was based on the weight prior to the first brood, regardless of whether they graduated to a higher weight class during the breeding period.

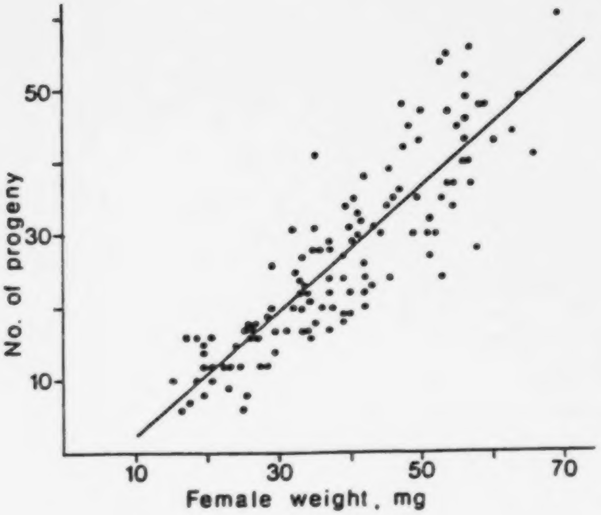


Figure VIII-2. First broods of *Trachelipus*: relationship between the post-parturient weight of females and the number of young released ($y = 0.859\ \mathrm{wt} - 6.434$; $r^2 = 0.77$).

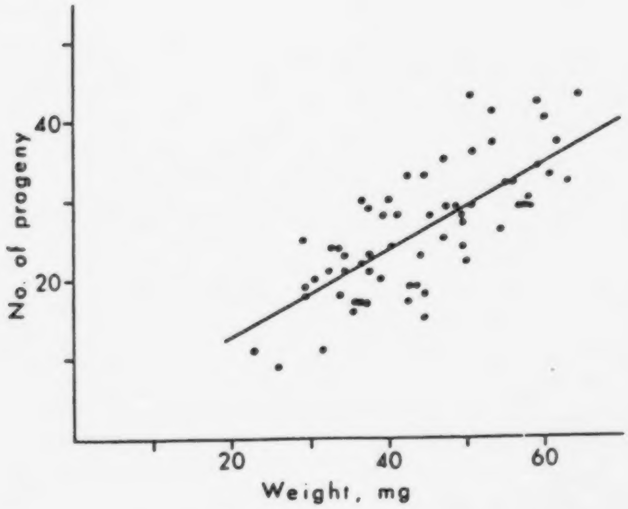


Figure VIII-3. Second broods of *Trachelipus*: relationship between post-parturient female weight and number of young released ($y = 0.538\ \mathrm{wt} + 1.154$; $r^2 = 0.47$).

TABLE VIII-4. SECOND BREEDING PERIOD OF Trachelipus FEMALES REARED AT CONSTANT TEMPERATURES.

		Temperature °C		
Days since 1st breed. period		15.6	21.0	26.7
(Mean ± S.D.)		136.3±30.8	115.2±29.7	140.5±35.8
No. alive		33	20	23
No. producing	brood 1	31	17	13
	brood 2	11	12	8
	brood 3	0	0	5
	brood 4	0	0	1

Note: No. alive: total number of females, of approximately the same weights as the breeders, that were alive through the second breeding period without reproducing.

McQueen (1976c) obtained an r^2 of 37% for this correlation. Fecundity is indeed variable, but some of that variability may be due to observational error. At least in culture, females frequently cannibalize their young during the first 24 hours following brood release. For example, when females kept at 21°C were observed twice a day, and were removed as soon as the last progeny had emerged, the relation between number of young in the first brood and weight gave an r^2 of 91%. The correlation was not as good for second broods, nor was it the same at all temperatures.

Second broods yielded fewer young than the first at 15.6°C ($t = 2.433$, d.f. = 30, $P < 0.05$) as well as at 21°C ($t = 2.866$, d.f. = 36, $P < 0.01$). At 26.7°C mean number of young in first and second broods were virtually equal, due to females that underwent a sterile molt between broods and were able to produce more young the second time. Heeley (1941) and Paris and Pitelka (1962) reported smaller second broods in other isopod species as well.

After summarizing over all temperatures, regression lines were obtained for first (Fig. VIII-2) and second broods (Fig. VIII-3). The slopes differ significantly ($t = 2.024$, d.f. = 179, $P = 0.05$).

TABLE VIII-6. PERCENT UNSUCCESSFUL BROODS IN THE FIRST PERIOD OF Trachelipus, PER WEIGHT CLASS AND TEMPERATURE*

	Pre-brood	Brood 1		Brood 2		Brood 3	
T°C	weight (mg)	n	% unsucc.	n	% unsucc.	n	% unsucc.
15.6	<30	22	18.2	1	0.0	0	--
	30-50	33	9.1	12	8.3	0	--
	>50	11	18.2	10	20.0	0	--
21.0	<30	18	5.6	0	--	0	--
	30-50	20	0.0	11	0.0	0	--
	>50	18	5.6	10	10.0	0	--
26.7	<30	31	9.7	9	11.1	0	--
	30-50	27	7.4	36	11.1	20	10.0
	>50	7	14.3	12	25.0	5	0.0

*Weights are those prior to each of the consecutive broods, so that success of a brood relates to the weight of the female carrying it.

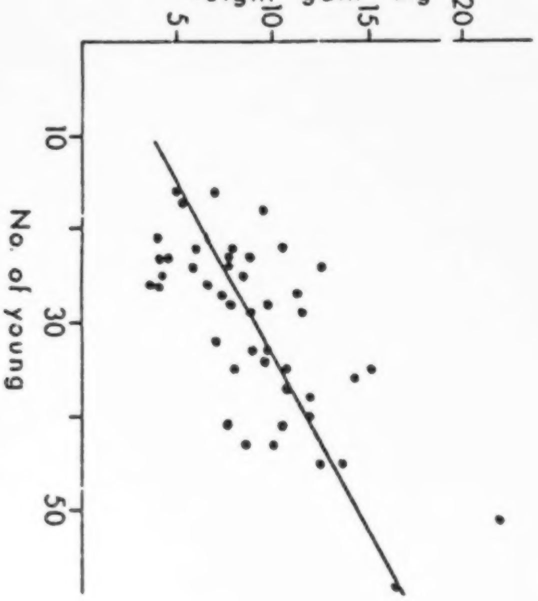


Figure VIII-4. Relationship between weight gained during gravidity and the number of young produced. Weight gain = maximum recorded weight - initial gravid weight ($y = 0.264x + 1.154$; $r^2 = 0.47$).

Brereton (1957) noted that viability of eggs of *Porcellio scaber* was about 82%, and Paris and Pitelka (1962) found a brood pouch mortality of 7 to 8% in *Armadillidium vulgare*. In *Trachelipus*, no checks were made for the presence of undeveloped eggs in the brood pouch after release. Any brood pouch mortality would already be included in estimates of fecundity which, strictly speaking, are estimates of natality (the number of live young actually released by a female). But there were incidences of unsuccessful broods in which the entire batch of eggs failed to develop. These eggs were actively expelled after having been carried for varying lengths of time, or remained in the pouch until being case off with the post-parturient molt. As observed by Hatchett (1947), morbid ova were almost always eaten by the female.

Table VIII-6 shows that the occurrence of faulty broods in the first breeding period was lowest at 21°C, and that, overall, females in the 30-50 mg class bred most successfully.

During gravidity, *Trachelipus* females gained weight rapidly as the eggs developed. Weight increases ranged from 313 to 22.1 mg (or 8 to 28% of the weight immediately after a brood molt). Maximum weights were usually reached in the early fourth quarter of the brood-carrying period. A linear relationship between weight gain and number of young could be shown to exist ($t = 6.183$, d.f. = 44, $P < 0.001$), with a correlation coefficient of 0.68 (Fig. VIII-4).

TABLE VIII-7. NUMBER OF DAYS NEEDED BY *Trachelipus* FEMALES TO REACH THE FINAL MEAN WEIGHTS (±S.D.) OF FIVE WEIGHTS CLASSES[1].

	Temperature °C					
Weight class (mg)	15.6		21.0		26.7	
0.5-5.0	167		79		43	
	5.0±1.3	10	5.0±1.3	12	5.0±1.6	44
5.01-12.0	57		39		19	
	12.0±4.0	10	12.0±3.2	22	12.0±2.2	44
12.01-30.0	151		61		40	
	30.0±9.7	10	30.0±6.5	22	30.0±6.3	44
30.01-50.0	170		92		76	
	50.0±5.3	6	50.0±4.6	22	50.0±5.6	22
50.01-80.0	260[2]		161[2]		138	
	65.0±2.9	7	71.0±6.1	7	80.0±5.5	14

[1] In italics: number of replicates alive at the time final mean weights were attained.

[2] Estimated from growth part way through the weight class; 15.6°C: 15 mg gain in 130 days; 21°C: 21 mg gain in 110 days.

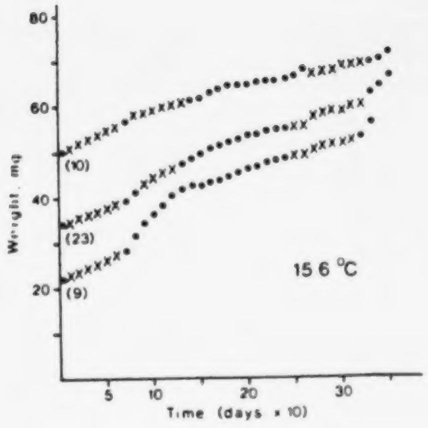
GROWTH

The time spent in gravidity, when no size increase through molting is possible, represents a delay of normal growth which is resumed with occurrence of the last post-parturient molt. Figure VIII-5 shows the long-term growth of breeding females. Almost all individuals happened to fall with in three specific weight ranges after their first brood release, and were grouped according to these weights: <30 mg (very small adults, 30-40 mg, and 50 to 60 mg. The data were synchronized such that day 10 was the day of the first brood molt for all replicates. The temporary weight gain during gravidity was ignored, and all 10-day mean weights were obtained by linear interpolation between actually recorded weights (at varying intervals of 8 days to 3 weeks).

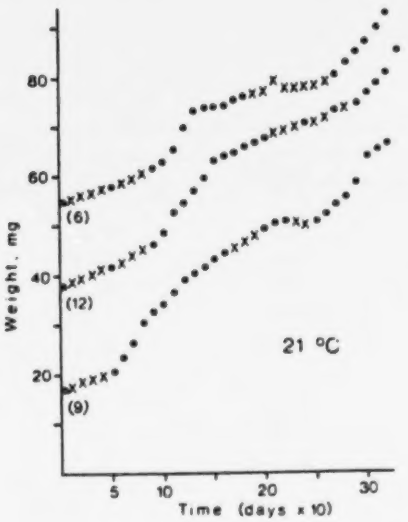
The delaying effect of reproduction on weight increase became most obvious at 21°C (Fig. VIII-5b): The first breeding period was followed by a time of rapid weight gain, a pattern repeated in the second breeding period. At all temperatures, growth following the first breeding period was most rapid in the smallest females. Only mean weights without confidence limits are given in these figures, because the individuals in each group were not all of the same weight initially. The largest standard deviations were recorded toward the end of the observation period, and ranged then from 12 to 19 percent of the means; standard deviations of mean weights on day 0 were only slightly lower.

Attempts were made to rear groups of females through each of the four major weight classes in order to obtain temperature-dependent growth rates without breeding interference. But many of the post-parturient females isolated for growth observations, whether field-collected in the fall or laboratory-reared, produced eggs again before having reached the upper limit of a given weight class. And the time needed to rear prejuveniles all the way to large adults was found to be prohibitive, especially at lower temperatures.

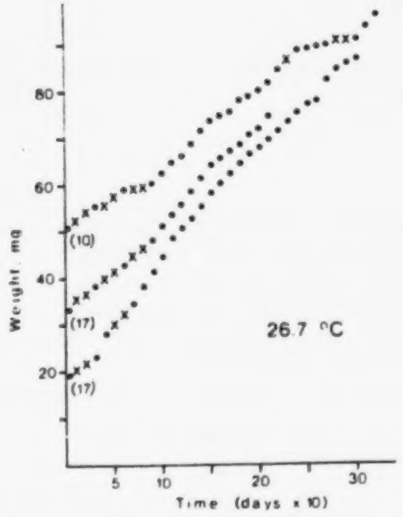
Finally, records of individual females were selected from a number of different observational series. Females were chosen only if they had reached the lower limit of a weight class after the last post-parturient molt, and had come at least close to the upper limit before breeding again. It was then possible to calculate the number of days needed to pass through each of the weight classes, i.e. to determine the day on which mean weights of 5.0, 30.0, 50.0 and 80.0 mg were attained (Fig. VIII-6). In the more detailed data presented in Table VII-7, standard deviations of final mean weights were included since all replicates per weight class had the same initial weight.



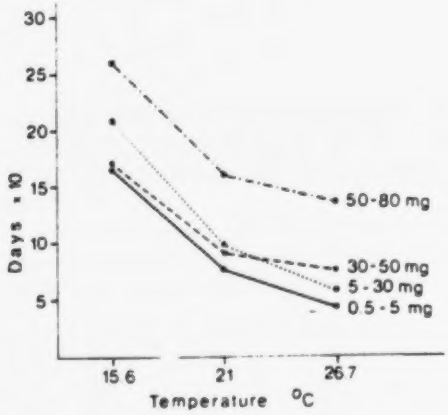
5a



5b



5c



6

Figure VIII-5a, b, c. Mean weights at 10-day intervals of breeding *Trachelipus* females reared at three temperatures. Crosses replacing dots indicate that 40 percent or more of all individuals were carrying broods. At each temperature, the replicates were grouped according to female weights after the first brood release: <30 mg, 30-40 mg, and 50-60 mg. Numbers in parentheses: number of replicates at the beginning of observation.

Figure VIII-6. Number of days spent by *Trachelipus* females in each of four weight classes, at three constant temperatures.

TABLE VIII-9 PERCENT MORTALITY OCCURRING EITHER DURING GRAVIDITY OR DURING THE POST-PARTURIENT MOLT OF BREEDING Trachelipus FEMALES.

T°C	Weight (mg)	Percent Mortality Brood 1	Brood 2	Brood 3
	<30	18.2	0.0	--
15.6	30-50	9.1	8.3	--
	>50	18.2	20.0	--
	<30	0.0	--	--
21.0	30-50	0.0	0.0	--
	>50	5.6	10.0	--
	<30	0.0	11.1	--
26.7	30-50	3.7	5.6	10.0
	<50	0.0	8.3	0.0

Note: As in Table VIII-6, weights are those prior to each of the consecutive broods.

TABLE VIII-8. CUMULATIVE TOTAL MORTALITY OF NON-BREEDING Trachelipus, IN PERCENT OF ALL INDIVIDUALS OBSERVED THROUGH EACH OF THE FOUR WEIGHT CLASSES (ONLY THE LOWEST CLASS INCLUDES MALES AND FEMALES, IN UNKNOWN PROPORTIONS.

Wt. class (mg)	Temperature °C 15.6		21.0		26.7	
0.5-5.0	20.0	*40*	10.0	*30*	7.0	*100*
5.01-30.0	19.0	*21*	8.7	*23*	11.5	*52*
30.01-50.0	29.4	*34*	12.1	*33*	14.0	*43*
50.01-80.0	--		40.0	*15*	48.9	*45*

Note: In italics: number of replicates.

TABLE VIII-10. SUMMARY OF BOARD COLLECTIONS OF *Trachelipus* IN 1978.

	Collection date												
	4/7	4/25	5/2	5/18	5/30	6/16	6/27	7/10	7/28	8/8	8/30	9/28	11/1
Total Number Collected	238	132	89	114	53	114	193	85	114	106	274	180	150
No. Females	109	70	28	39	33	65	62	30	41	26	69	58	72
% Females	52.4	55.5	39.4	57.4	66.0	61.3	61.4	60.0	61.2	54.2	52.7	60.4	52.9
No. Females ≥ 12 mg	87	63	24	21	30	57	51	24	39	20	22	50	65

Note: Total numbers include prejuveniles; numbers of females and percent females are based only on animals in which sexes could be distinguished [% females = no. of females/(females + males)].

The necessity to discontinue observations arose at a time when animals kept at 15.6 and 21°C had not yet reached 80 mg. The duration of these classes was therefore estimated based on the number of days needed to attain weights of 65 mg (15.6°C) and 71 mg (21°C). These were linear estimates; actual durations would probably have been longer, since the non-linearity of growth in large adults has been shown by McQueen (1976c).

MORTALITY

A distinction was made between brooding and non-brooding female survivorship rates. The data for non-reproductive Trachelipus were derived from a number of different observational series, all using isolated individuals. Records of adults were selected if the animals had entered a size class after a post-parturient molt.

Table VIII-8 shows cumulative mortality percentages per temperature and size class. The data are based on weight only--e.g. they concern animals that died before having reached the upper limit of their class, irrespective of how many days they were actually alive. For all but prejuveniles, 21°C was the most favorable temperature. The data for adults agree well with McQueen's (1976c) results, which determined maximum survivorship to lie between 20 and 25°C. But at 15.6°C prejuveniles incurred less mortality, and juveniles greater mortality, than the populations studied by McQueen at a comparable temperature of 15°C.

Mortality increased with increased female weight. At 15.6°C very few animals ever reached 80 mg, so that reliable percentages could not be calculated. At 21 and 26.7°C some individuals continued to grow to weights of about 100 mg, but almost none of the field-caught females exceeded estimated weights of 80 mg. This may indicate that field conditions do not allow survival beyond 80 mg, or if so, that those animals form only a minute segment of the population.

As previously observed by Hatchett (1947), Trachelipus females frequently died during a molt, especially while trying to shed the anterior half of the exoskeleton. Paris and Pitelka (1962) agreed with Geiser (1934), who explained the preponderance of adult males over adult females by a greater female mortality during brood molts. In the present study, "breeding mortality" included females that died while carrying brood, those that died while expelling morbid ova, and those that did not survive the post-parturient molt.

Table VIII-9 shows percent mortality connected with each brood. At 15.6°C all deaths were connected with non-developing eggs; at the two higher temperatures, some females survived faulty broods (see Table 6) and produced a second, successful, brood. Thus brooding deaths occurred most commonly during or immediately after unsuccessful broods. Only 16 percent of all brooding mortality was connected with unsuccessful post-parturient molts.

RESULTS: FIELD OBSERVATIONS

NUMBERS IN THE FIELD

Table VIII-10 summarizes the capture totals and the data pertinent to the female population. As in 1977 (Chapter IX or Snider 1979) the sex ratio during the 1978 sampling season was generally around 60% females, and not nearly as variable as that observed by McQueen (1976c). Also shown are the number of females estimated at $\geq$ 12 mg in weight, which was the lower limit set for breeding ability in this study. McQueen (1976c) suggested that sexual maturity is reached in the 20 to 30 mg range; the present estimate therefore appears conservative, but individuals estimated at 12 to 24 mg were found to make up a sizeable segment of the reproductive population in the orchard.

As pointed out by McQueen (1976c), numbers of animals captured from boards vary greatly, mainly as a function of weather conditions prior to the collection day, and do not reflect true density. In order to obtain a seasonal point-estimate, population density was assessed in late October, 1978; 20 block samples, 15 x 15 x 15 cm, from under tree canopies and 20 from alley areas were handsorted for isopods. Mean density ± S.E. was estimated at 107 ± 26.8 and 60 ± 19.7 individuals per m^2 respectively. These differing densities are also reflected in the number of individuals found under boards in the two habitat types: boards under canopy cover harbor significantly more animals than those in alleys (Snider 1979).

Population size of Trachelipus seems quite low when compared to an estimate of $538/m^2$ for Armadillidium vulgare in California grassland (Paris and Pitelka 1962). Aside from species specific differences, one reason for low density could be found in the degree of disturbance at the orchard site--mowing by tractor and human trampling being the most obvious.

Using the number of animals collected from boards on November 1 (a board covering an area of 525 cm^2), one would arrive at a mean density ± S.E. of 112.8 ± $50.9/m^2$ for the area under trees and 125.3 ± $72.8/m^2$ for alleys between trees. The estimate of density under canopy is close to that derived from handsorting. That in alleys is about twice the actual density. The very large standard errors reflect the fact that large aggregations of Trachelipus often form under individual boards.

Further handsorting at different times of the season is clearly indicated. It would allow the determination of the degree of "attractiveness" of the boards as it relates to weather conditions, characteristics of the habitats, and to the true density of the population in the surrounding areas.

POPULATION SIZE STRUCTURE

In Figure VIII-7 weight distribution over the four major classes is expressed as percent of total catch of females per collection date. Advancement from one class to the next is clearly defined in only a few instances; e.g., movement into the highest weight class in mid-summer; disappearance of these > 50 mg animals in late summer and their reappearance in the fall during the brief period of growth before the onset of winter.

McQueen (1976a), using mark-recapture methods on a population of Porcellio spinicornis, noted that capture efficiency varied with sex as well as with size of individuals. In the present study, collections from April 7 to June 16 yielded variable numbers of prejuveniles, with an apparent peak on May 18. Since no recruitment took place at that time, increasing prejuvenile captures may best be explained by differential response of large and small animals to temperature and moisture conditions, at least in April and early May. Beyond that time, it is obvious that rapid growth is responsible for removing individuals from the prejunveile contingent and shifting them into the juvenile and young adult classes.

The growth pattern can be shown more clearly if each of the four classes is broken down to three subclasses (Fig. VIII-8). The prejuvenile peak apparent in Fig. VIII-7 in May can now be shown to consist of overwintered animals belonging in the heavier prejuvenile groups, which have outgrown the 5 mg limit by the time brood release begins. New recruits appear in late June

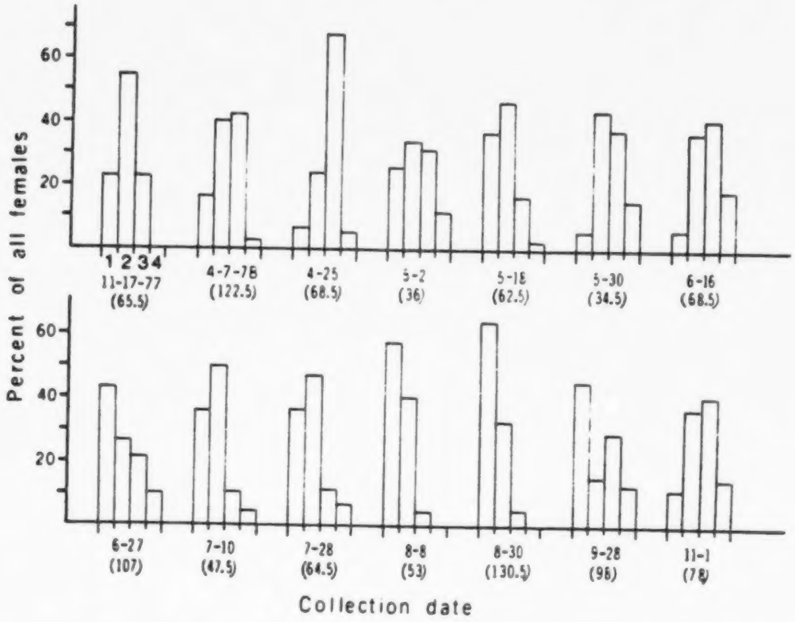


Figure VIII-7. Weight distribution of the *Trachelipus* field population, in percent of all females captured per date. Total numbers (in parentheses) include half of the prejuveniles plus all identifiable females caught. Weight class definitions: 1 = 0.5-5.0 mg; 2 = 5.01-30.0 mg; 3 = 30.01-50.0 mg; 4 = >50.0 mg.

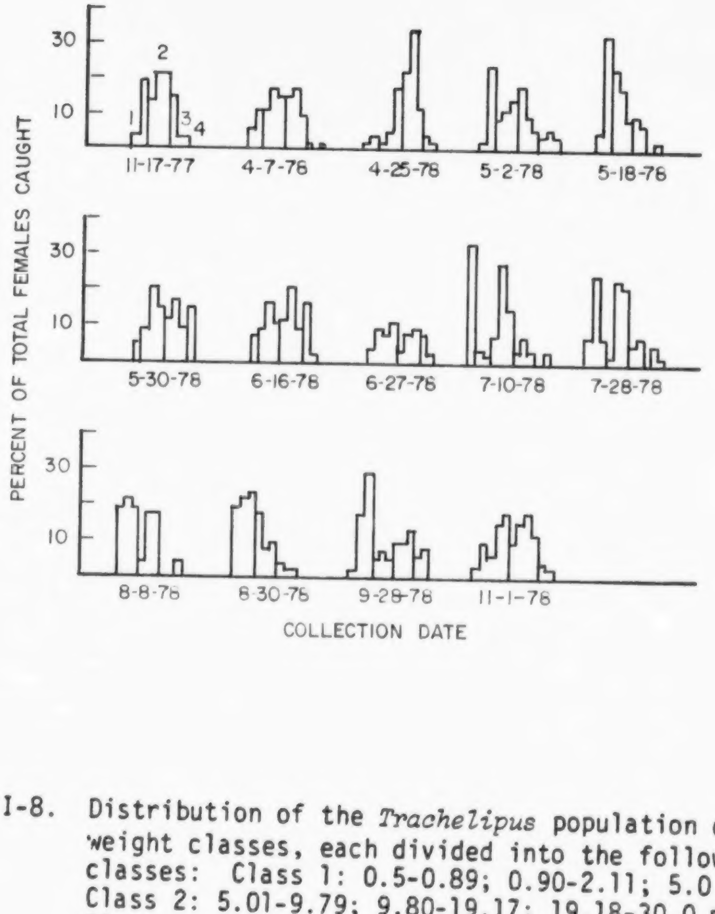


Figure VIII-8. Distribution of the *Trachelipus* population over four weight classes, each divided into the following subclasses: Class 1: 0.5-0.89; 0.90-2.11; 5.0 mg. Class 2: 5.01-9.79; 9.80-19.17; 19.18-30.0 mg. Class 3: 30.01-35.57; 35.58-42.17; 42.18-50.0 mg. Class 4: 50.01-59.28; 59.29-70.29; >70.29 mg. Data are given as percent of all females caught. Total numbers as in Fig. 7.

and graduate through the prejuvenile class during July. A second prejuvenile peak then occurs, with a subsequent rise in juvenile numbers apparent in late August.

In analogy to the population studied by McQueen (1976c), cohorts of recruits can be followed through the year. In April and May, the last individuals of the 1977 cohort graduate to juveniles and adults. The heaviest females found in April may be the remainder of the 1976 cohort (2 year-olds), but individuals also grow into the >50 mg class during June. In July, both medium-sized and large adults begin to dwindle, indicating that the majority of the 1977 cohort (1 year-olds) and probably all of the 1976 cohort (2 year-olds) die at that time. The 1978 cohort replenishes the heavier weight classes during fall growth. By early November, the bulk of the population consists of young adults and adults, with an overall weight distribution reminiscent of that found in April.

BREEDING PERIODICITY

Collections in April and early May never yielded gravid females. They first appeared on May 18; by late May, over 70 percent of the females were gravid.

During June the population rapidly reached its full reproductive potential. The solid line in Fig. VIII-9 includes all individuals "in breeding condition," i.e., both those carrying brood and those which had recently released their progeny (oostegites still present). For comparison with McQueen's (1976c) Canadian Trachelipus population, Fig. 9 also shows breeding percentages based only on females actually carrying brood; the two peaks are about one month apart, reaching 86 and 60 percent of all females of potential breeding weight. McQueen's field counts of gravid females were thus closely replicated, concerning both the timing of reproduction and the percentage of breeders in the population.

By assigning brood-carrying females to three weight classes, it can be shown that reproductive activity is initiated by the heavier females, and that individuals weighing <30 mg gain in relative importance toward the latter part of the season (Fig. VIII-10). Larger females exhibit a shift into a second brood. Smaller females appear to come into breeding condition gradually, as individuals attain reproductive size during summer growth. By July, their importance begins to exceed by far that of the heavier females.

This breeding pattern is substantiated by the pattern of brood release. Table 11 differentiates between two states of breeding condition: broods developing in the pouch, and empty oostegites prior to the post-parturient molt. The first release-pulse (late June to early July) is due mainly to females >30 mg in weight; by late July, these again carry brood. In small females, first and second broods are not clearly distinguishable. Those that were able to breed relatively early in the season probably breed a second time, but may by then have entered the next higher weight class.

Table VIII-11 also shows that 100 percent of all females >30 mg in weight carried broods by late May; and that the small females reached a reproductive peak in July, when 93 percent of all captured females in this class were in breeding condition.

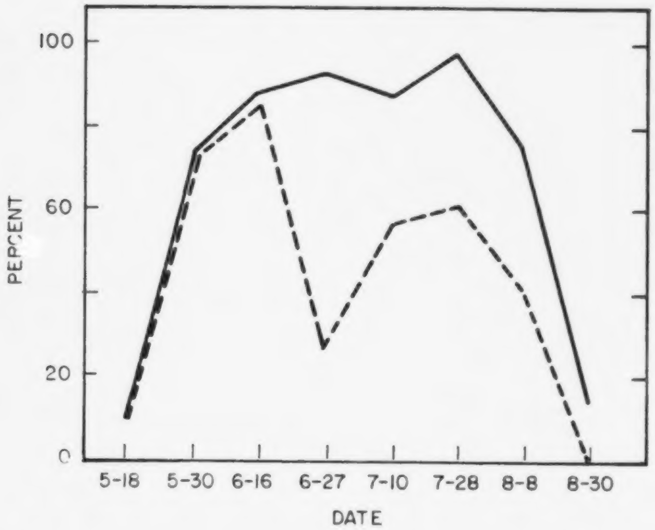


Figure VIII-9. Breeding periodicity of *Trachelipus* in the field: of all females ≥ 12 mg, percent in breeding condition. Solid line: females with empty oostegites included; broken line: only individuals actually carrying brood are counted.

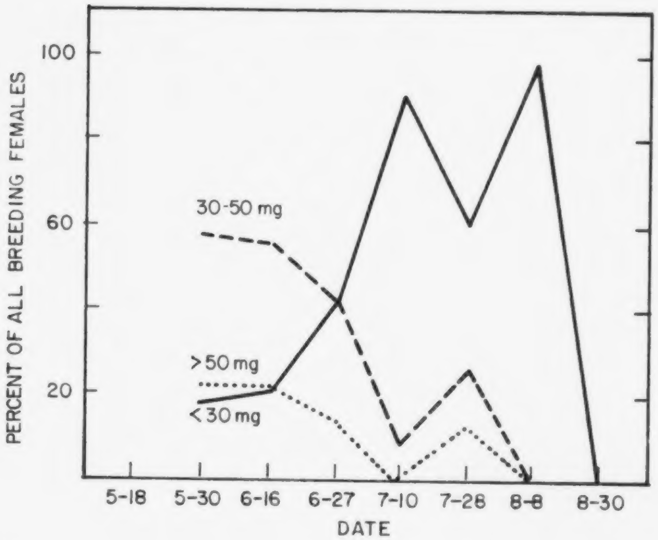


Figure VIII-10. Weight structure of the breeding segment of the *Trachelipus* field population, in percent of the total number of females carrying brood on each collection date.

Table VIII-11. Breeding periodicity of Trachelipus females in the field, categorized by estimated weights.

Date	12-30 mg no. in breed. cond.	BR %	REL %	30-50 mg no. in breed. cond.	BR %	REL %	>50 mg no. in breed. cond.	BR %	REL %
18/5	1	100	--	1	100	--	0	--	--
	10			*10*			*1*		
30/5	4	100	--	13	100	--	5	100	--
	12			*13*			*5*		
16/6	10	100	--	28	100	--	12	91.7	8.3
	17			*28*			*12*		
27/6	15	64.3	35.7	22	27.3	72.7	10	20.0	80.0
	19			*22*			*10*		
10/7	16	68.7	31.3	3	33.3	66.7	2	--	100
	18			*5*			*2*		
28/7	27	51.9	48.1	7	85.7	14.3	4	75.0	25.0
	29			*7*			*4*		
8/8	11	54.5	45.5	2	--	100	0	--	--
	18			*2*			*0*		
30/8	1	--	100	2	--	100	0	--	--
	16			*6*			*0*		

Note: Total numbers (italics) captured in each weight class. BR: broods carried; REL: broods recently released, oostegites still present.

It is likely that individuals >30 mg had been fertilized the preceeding fall and were able to set broods as soon as spring temperatures triggered molting activity. The lag in the appearance of small gravid females may be partly due to a lesser "inclination" to breed at lower temperatures. But it becomes evident that overwintered prejuveniles, and juveniles of low weight, grow to young adults in May and June, and then begin to breed; and that their contribution to population recruitment is relatively important, even though each individual may produce only a small number of progeny.

Paris and Pitelka (1962) observed a very similar distribution of size (age) classes in A. vulgare: early breeding was carried out mainly by 2- and 3-year old females, and one-year old classes contributed increasingly to recruitment as the season progressed.

DISCUSSION

There are obvious similarities between the Trachelipus population at the orchard site and the Canadian population studied by McQueen (1976c). The fate of each cohort, the periodicity and extent of breeding activity, and the probable maximum life span, are virtually identical. Where there are discrepancies, they may well be attributable to disparities in methodology rather than to differences inherent in the populations.

A case in point can be found in the weight distribution of breeding females and the determination of potential reproductive size in field populations. McQueen (1976c) weighed captured animals directly, while orchard Trachelipus were measured and their weights estimated. Since gravidity increases weight, weighed gravid females would be assigned to heavier classes than warranted by size. As a result, the lower weight limit for potential reproduction would appear to differ in the two populations.

Survivorship characteristics of the two populations do not seem fundamentally different, temperatures around 20°C being the most favorable for all weight classes. Considering that rearing methods were not identical, it is not surprising that there are divergent results--e.g., in McQueen's observations, a higher mortality of prejuveniles at 15 and 25°C and a lower mortality of juveniles 15°C. If mortality patterns were inherently different in either population, the observed similarity in seasonal weight distribution could only arise if other characteristics differed as well. None of the pertinent data suggest this to be the case, although the number of offspring recorded for Michigan Trachelipus was higher than that observed in Canadian stock. The regression obtained by McQueen (1976c), applied to the females observed in the present study, would underestimate natality rates for both first and second broods. Here again, if both studies had used either gravid or nonbrooding weights, the regression lines would probably have been quite similar.

McQueen's (1976c) sampling technique did not enumerate individuals weighing <5 mg, but the 0-10 mg class shown in his diagrams was equally as prominent during May as the corresponding weight classes in the orchard population. In both cases, the appearance of new recruits was sharply delineated. Although growth rates in our laboratory stock were slightly lower than the rates observed by McQueen, growth of the two field populations seemed comparable, exhibiting similar patterns of cohort advancement.

Clearly, temperature is a major factor regulating growth, mortality and reproductive timing of Trachelipus. McQueen (1976c) addressed the question of population limitation; unlike P. spinicornis (McQueen and Carnio 1974; McQueen 1976a, b), Trachelipus did not appear to be limited by climatic conditions in the Ontario region, since the population expanded over a three-year period. Comparable data are not available for the Michigan population, since neither mark-recapture programs nor repeated density estimates were attempted. The different nature and past history of the sampling sites alone would make such comparisons speculative. Overall, the populations behaved similarly. What the full growth potential of Trachelipus populations might be, would have to be investigated in contrasting habitats where factors other than climatic conditions could be quantified and compared. A periodically managed orchard with a relatively bare floor stratum probably offers less protection and fewer resources than, for instance, an undisturbed woodlot.

CHAPTER IX

THE EFFECTS OF AZINPHOSMETHYL ON A POPULATION OF *Trachelipus rathkei* (Isopoda)

This Chapter reports the results of the detailed study of azinphosmethyl effects on an example soil/litter invertebrate population. Trachelipus (Tracheoniscus) rathkei (Brandt, 1833), the only isopod species present at the experimental site, was one of the organisms selected for intensive study in both the field and the laboratory. McQueen (1976c) successfully constructed a simulation model of a Trachelipus population in Ontario, Canada, and provided valuable information and guidelines for the present study. His concern has been the problem of limitation in terrestrial isopods (reviewed in McQueen 1976a, b), but he could not pinpoint a definite limiting factor in the case of T. rathkei.

Although climate patterns appear to regulate some isopod species (Sutton 1968; McQueen and Carnio 1974; McQueen 1976a, b), annual temperature conditions did not limit population growth of T. rathkei, leaving pathogens and drought as possible alternatives (McQueen 1976c).

In disturbed environments, given that T. rathkei will move until its microclimatic requirements are satisfied (White 1968), factors connected to management by man seem to gain in importance. Trampling, for instance, can play a major role in population reduction (Duffey 1975), and susceptibility of the species to pesticides may curtail its ability to maintain viable population levels. The effects of chemical stress due to azinphosmethyl, in an orchard system, are the subject of the present report.

THE FIELD SITE

The apple orchard where these investigations were carried out lies in the vicinity of Grand Rapids, Michigan, in Kent County. Planted over 20 years ago, it had been left untended since then.

In spring of 1976, the trees were trimmed, understory brush was removed, and the area was mown. Trimming has been repeated every spring; the ground cover has been mown again two or three times every season, and the clippings have been left on the ground.

A survey of the ground cover by the line-transect method (Cox 1974) was carried out in 1976. Rather than determining species composition, "cover type categories" were established and their importance values calculated. Moss intermingled with litter, and moss-litter-broadleaf complexes, were by far the most prevalent in the entire experimental area.

Seven plots were originally delineated, one of them a control separated from sprayed areas by an unmanaged buffer strip. Pit-trapping in 1976 had yielded only few isopods in the control plot, probably because isopod activity was curtailed during this particularly dry summer. But in order to safeguard against possible low densities and ensuing difficulties in data analysis, a second control plot was set up in early 1977. A total of eight plots were than in existence; of these, four were sampled for isopod populations throughout 1977-1978; plots 2 and 5 were treated with azinphosmethyl, plots 7 and 8 were control. Plots 2, 5 and 7 were in their second year of use, plot 8 in its first.

The plot boundaries were delineated by aluminium core stock (fencing) embedded in the ground to a depth of 8 cm, and protruding to a height of 20 cm. The fencing followed the contour of the land and was meant to enhance channelling of runoff for collection of water samples at the bottom of the slopes. However, not all plots were completely enclosed. Immigration of flightless invertebrates, across unfenced boundaries as well as across the fence, should be kept in mind as a mechanism of population replenishment, but was not quantitatively assessed.

Azinphosmethyl (50% wettable powder) was applied at the rate of 1.1 kg/ha (1 lb a.i./acre), using a low-volume, low pressure tractor-drawn spray rig similar to one developed by Howitt and Pshea (1965). Pesticide application dates in 1976 and 1977 are given below:

1976: July 2, July 15, July 28, August 17.
1977: May 26, June 16, July 7, July 22, August 12.

METHODS AND MATERIALS

Boards were cut from weathered barn wood, to a uniform size of 35x13 cm and 2 cm in thickness. They were positioned in the field such that the area underneath them was fairly even, and were weighted down with stones. Plots 2, 5 and 7 each had 10 boards, plot 8 contained 20. In each plot, half were placed under tree canopies and half out in the alleys between tree rows. The first collections were made about two weeks after positioning the boards.

Animals were collected both from the underside of the boards and from the debris and soil crumbs beneath. They were sexed and measured in the laboratory and returned to the boards they came from.

Size measurements were done under a dissecting microscope with an ocular micrometer. Head capsule width and width of the last thoracic segment were recorded. First and second instars are recognizable by absence of the seventh thoracic segment. Third instars possess a seventh segment, but it is relatively narrower than in older stages. Occurrence of these young stages, and of the breeding condition of adult females, were noted.

RESULTS

The position of the boards with respect to tree cover had a significant effect on the number of individuals recovered (Fig. IX-1). *T. rathkei* were more numerous under tree canopies on almost all dates.

In plot 8, not all boards were sampled at all times. The mean number of animals per board under trees was compared to the mean of those found in alleys (over all sampling dates): variances being unequal, Behrens' (1929) t-like test statistic and Welch's (1938) critical values were applied. With $P < 0.001$, boards under trees harbored significantly more isopods than those in alleys. In plot 7, replication being equal on all dates, a paired t-test on mean number of animals per board per collection date again showed the same results ($P < 0.01$). Corresponding data from sprayed plots were not analyzed because of the low number of individuals collected through the year.

Tree shade with concurrent lower temperatures and higher humidity, as well as less physical disturbance in the area around the trunk that cannot be mown, may all have contributed to higher densities under the canopy cover.

SEX RATIOS IN THE FIELD

Young individuals cannot be sexed with certainty until the head capsule

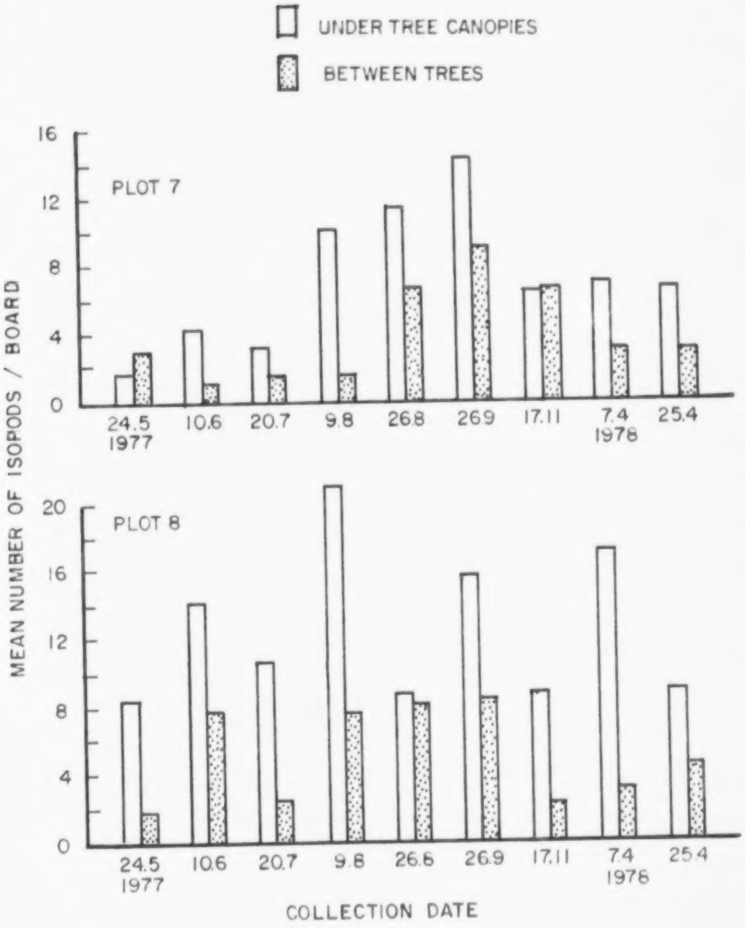


Figure IX-1. Mean number of *T. rathkei* collected from boards placed underneath tree canopies and from those in alleys between trees.

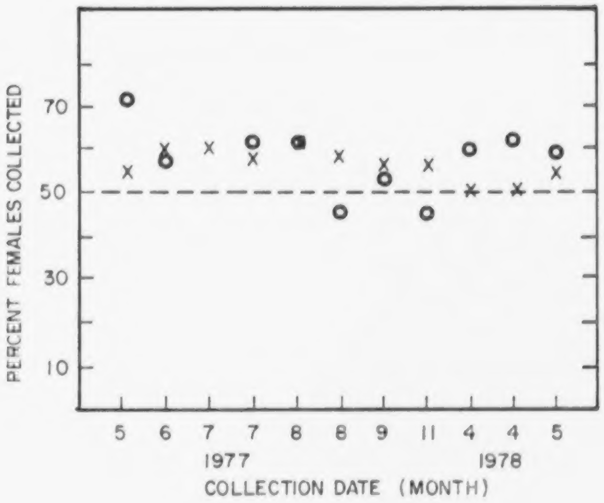


Figure IX-2. Percent females captured, of the total number of *T. rathkei* that could be sexed; exact collection dates as in Fig. 1 Symbols: O = Plot 7, X = Plot 8.

measures about 1.1 mm in width. Fig. IX-2 shows the percent females, of the total number of sexually recognizable animals captured, in plots 7 and 8. The data are not as variable as the percentages given by McQueen (1976c). However, the recurrence of a sex ratio of close to 50% strongly supports McQueen's suggestion that differential behaviour rather than differential mortality, i.e. higher mortality of males (Brereton 1957), is the cause of the observed sex ratios in the field.

EFFECT OF AZINPHOSMETHYL ON NUMBERS OF INDIVIDUALS

The mean number of animals collected per board and date are summarized in Table 1. The isopod populations in sprayed plots were apparently drastically reduced during the 1976 spray season and did not recover during 1977.

Paired t-tests were used for all comparisons between plots. The two sprayed plots did differ significantly ($P < 0.05$). It should be noted that the upper edge of plot 2 was not fenced in the usual way, but abutted to a sparse hedgerow. The nearest boards were at least 6 meters away from it, but immigration along that edge cannot be ruled out. Plot 5 was completely fenced in.

Plots 7 and 8 also differed considerably ($P < 0.01$); the relatively greater number of animals recovered from plot 8 may be attributable to the fact that this second control plot had only been established in the spring of 1977, while plot 7 was in its second year of use. Factors such as compaction by human trampling and mowing would not have come into play to the same extent in these two plots.

Keeping in mind this past managerial history, the sprayed plots were each tested against plot 7, the older control (plot 2: $P < 0.01$; plot 5: $P < 0.01$). Thus the mean number of individuals collected was significantly smaller in the two sprayed plots.

Table IX-1. Mean number of _Trachelipus rathkei_ per board on each collection date

Date	Plot number			
	2	5	7	8
24.5. 1977	0.3	0	1.8	5.1
10.6.	0.3	0	2.4	6.8
20.7.	0.1	0	2.3	5.0
9.8	0.2	0.2	5.6	7.2
26.8.	1.6	0.2	9.0	8.3
26.9.	*	*	11.6	17.6
3.11	1.7	1.0	*	*
17.11.	0	0.6	6.3	5.3
7.4. 1978	3.7	2.4	4.8	10.0
25.4.	3.4	2.2	4.6	6.6
16.5.	1.3	0.6	3.5	6.0

* denotes that no samples were collected on these dates.
Plots 7 and 8 are control, plots 2 and 5 were sprayed; plots 2,5 and 7 contained 10 boards each, plot 8 contained 20.

EFFECT OF AZINPHOSMETHYL ON POPULATION SIZE STRUCTURE

Captures from plots 7 and 8 (controls) and 2 and 5 (sprayed) were combined for a comparison of size structure within the populations. In his model of a Canadian Trachelipus [Tracheoniscus] population, McQueen (1976c) divided the population into three wieght classes: 0-5 mg (prejuveniles), 5-30 mg (juveniles), and > 30 mg (adults). In the present study, the animals were measured only. Five size classes according to head width, and based on life cycle observations of the psecies (to be published elsewhere) were established:

Class 1: head width 0.5 to 0.7 mm; this class encompasses the first three instars, approximately; progeny released by females between capture and return to the field were not included.

Class 2: head width 0.75 to 1.15 mm: sexes cannot be recognized with certainty in these animals.

Class 3: head width 1.2 to 1.4 mm; sexes are easily distinguishable, but the females do not contribute the bulk of the breeders (21% of the females collected in breeding condition had a head width of 1.3 to 1.4 mm).

Class 4: head width 1.45 to 1.8 mm; this class contains the majority of reproductive adults.

Class 5: head width 1.85 to 2.25 mm; such specimens were found only rarely throughout the season. This did not appear to be a result of the collection technique used. The orchard population may characteristically lack these large individuals, although they are relatively common in woodlot population mid-Michigan.

Fig. IX-3A shows the combined data from plots 7 and 8 (controls). Breeding starts in late May, and evidence of brood release is found in the increasing importance of size class 1 from July through August. As these young stages grow, they graduate to classes 2 and 3 which provide the bulk of the juvenile population in April and May of the following year. McQueen (1976c) and McQueen and Carnio (1974) estimated that prejuveniles-roughly equivalent to classes 1 and 2 combined - were seldom able to overwinter in Canadian populations of T. rathkei and Porcellio spinicornis. In the orchard population, over-winter mortality seems much less drastic; the survivors of late summer broods (gravid females were still found in late August) mature the following year and contribute to classes 3 and 4 during summer growth.

In contrast to this population continuity in control plots, Fig. IX-3B demonstrates that the sprayed plots, with rare exceptions, harbor an impoverished population of only large-sized individuals. Breeding females were found in May through July, but virtually none of the progeny could be located. Since the last spray application occurred in mid-August brood release in late summer and early fall apparently contributed a small number of young, which appear as classes 2 and 3 in spring of 1978.

During the spray season, however, the majority of newly hatched juveniles seem to have been eliminated by the presence of azinphosmethyl in their habitat. Toxicity experiments in the laboratory strongly support this assumption (see Chapter VIII). Briefly, adults are not susceptible to concentrations of much less than 10 ppm, but individuals belonging to class 1 are killed by exposure to contaminated soil at concentrations of 1 to 2 ppm. Soil samples from the experimental site, analyzed by gas-liquid chromatography generally do not exceed levels of 0.5 ppm; litter on the other hand frequently contains up to 35 ppm (Dr. Robert Kon, pers. comm.). Thus the impact of the pesticide would be greatest at the time of peak reproduction, during midsummer; but a skeleton population of recruits survives to carry over into the next year.

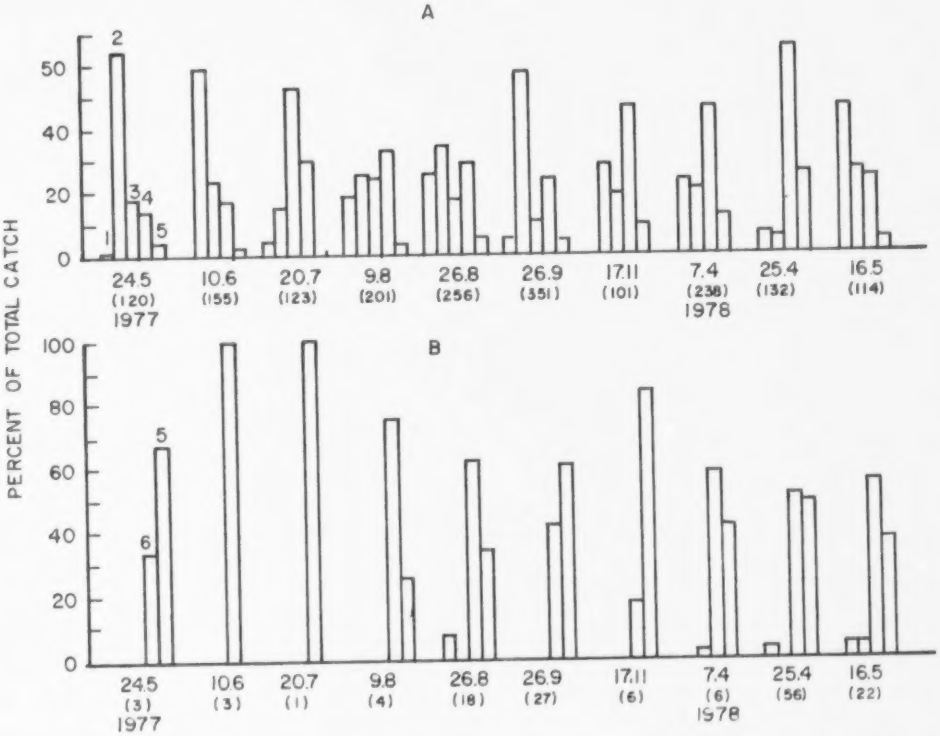


Figure IX-3(A,B) Size class distribution, in percent of total number captured per date, of *T. rathkei* populations throughout one year. A: control plots 7 and 8 combined. B: sprayed plots 2 and 5 combined. In parentheses: number of animals collected. See text for description of size classes. Errata in fig. 3B. Plot-number above the first column should be read 4 instead of 6. At 07.04.78 61 animals were collected.

DISCUSSION

Certain aspects of this study should be kept in mind in the discussion of results. One, that populations in sprayed plots had already been subjected to azinphosmethyl during the 1976 season. Data on their initial pre-spray state are not available, but there seems no good reason to assume that the population throughout the orchard (then not managed and not divided into plots) would have differed greatly, in density or structure, from area to area. And second, that the success of collecting individuals, especially very small ones, probably decreases as a function of decreasing density. No claim can be made that all animals present under the boards were actually located and collected.

The significant differences between the control plots might be explained by the different length of time each had been in use. The differences between the two sprayed plots are based on very few individuals, which may lead to an exaggerated view of pesticide effects because of low capture efficiency. But the absence of juveniles and even subadults (class 3) in sprayed plots is striking. The maximum life span of the species is two years in this climatic region (McQueen 1976c), and spring of 1978 represents the beginning of the third consecutive year of pesticide application. At that time, the reduced population in sprayed plots must represent survivors of the cohorts initiated in summer of 1977 (classes 2, 3 and 4) and possibly also in 1976 (large individuals of class 5).

It is conceivable that such a low-density population can maintain itself under stress of azinphosmethyl application, aided by heterogeneous distribution of the pesticide on the orchard floor, washout by rain, and surviving late-summer broods. Whether a lower limit of population density is ever reached beyond which population persistence is not possible, remains, unanswered until further data throughout consecutive years of pesticide application can be obtained.

CHAPTER X

A STUDY AND MODEL OF AZINPHOSMETHYL EFFECTS ON A POPULATION OF *T. rathkei*

INTRODUCTION

An extensive investigation of the effects of azinphosmethyl spray application in a Michigan orchard was begun in 1976. The field sampling program furnished the basis for a model of pesticide distribution and movement and also provided information on the impact of azphosmethyl on selected members of the invertebrate fauna of soil and litter.

It became obvious that one of the non-target organisms most affected was the isopod *Trachelipus rathkei* (Brandt), and the species was chosen for a detailed demographic model - an organism submodel intimately linked to the orchard-pesticde model mentioned above.

Ecobiological parameters, greatly enhanced by recent work on the demography of *T. rathkei* in Ontario, Canada (McQueen, 1976b), were obtained in both laboratory and field and are described in detail in Chapter VIII and in Snider and Shaddy (1980). In addition, successful linkage of the population model to the pesticide dynamics model necessitated knowledge of the susceptibility of the species to azinphosmethyl. Preliminary field observations to that effect were reported by Snider (1979) and in Chapter IX: substantiating data were obtained in laboratory experiments as well as through additional field sampling, and are included in this report.

T. rathkei Biology

A Summary of the Life Cycle

The biology of the species will be reiterated briefly, based on results from a two-year investigation carried out partly in the laboratory and partly in the field. Extensive information on the ecobiology of *T. rathkei* has recently been given by McQueen (1976c). In addition, McQueen and Carnio (1974), Carnio (1974), and McQueen (1976a, b) have compiled reviews encompassing physiology, behavior, and demographic patterns of terrestrial isopod species. Unless otherwise stated, the following summary is based on data presented by Snider (1979) and Snider and Shaddy (1980). Details of rearing and sampling techniques may be found those publications (Chapters VIII and IX of the report).

As did McQueen (1976c), weight classes were defined for *T. rathkei* females as a means of classifying population data. The two classes containing prejuveniles extend from a birth weight < 0.5 to 1.34 mg, and 1.35 to 5.0 mg. Individuals in the 5.01-12.0 mg class, termed juveniles, are not yet reproductive. Breeding is possible, however, for at least some of the females weighing ≥ 12.0 mg, and 12.01-30.0 mg class was defined as young adults. Those termed adult 1 weighted 30.01-50.0 mg; adult 2, which are nearing or in their second year of life, are brought together in a 50.0-80.0 mg class.

Eggs develop and hatch in the female's brood pouch, from which the young are released over a period of a few hours to about two days. Development time in the pouch is strongly influenced by temperature (51 days at 15.6°, 31 days at 21°, and 18 days at 26.7°C). Within 24 hours, the newly emerged young undergo their first molt, then begin to feed.

Through a series of molts, growth is achieved at temperature-dependent rates. By the time a weight of 5 mg is attained, males are distinguishable from females by the presence of a faint keel on the carpus of the seventh pair of legs. Intervals between ecdyses are short at first, but lengthen and become more irregular as the animals age; molting frequency also increases with rising temperature (unpublished data). As a measure of weight gain versus time and temperature, Table X-1 shows the number of days needed for *T. rathkei* to grow through each of the weight classes.

Table X-1. Number of days needed for *T. rathkei* to grow through each weight class at three temperatures. In parentheses: final mean weights ± S.E.

	Weight Class, mg			
T°C	0.5-1.34	1.35-5.0	30.01-50.0	50.01-80.0
15.6	70(1.34±0.11)	97(5±.4)	170(50.0±1.5)	260*(65.0±1.1)
2.0	39(1.34±0.10)	40(5±.4)	92(50.0±1.0)	16*(71.0±2.3)
26.7	23(1.39±0.04)	20(5±.2)	76(50.0±1.2)	138(80.0±1.5)

*Durations estimated linearly, based on the number of days needed to reach 65.0 and 71.0 mg; observations had to be discontinued at that point.

In the field, growth can be followed by analyzing the weight distribution of the population through the year. In April and May, up to 35 percent of the population consists of overwintered prejuveniles, probably late-born members of the recruits of the preceding year (cohort I). Older individuals of cohort I (released in June and early July) have reached juvenile and adult weights.

The bulk of cohort II arises from adults of cohort I, and from juveniles of cohort I after they have reached reproductive size during summer growth. During and after the breeding period, surviving cohort I females advance to weights exceeding 50 mg, overwinter, and enter their second reproductive period in May of the following year. By late summer, all of them seem to die out, at a time when the overwhelming bulk of the population consists of prejuveniles and juveniles of cohort III. By the end of autumn, cohort III has graduated to large prejuveniles, juveniles, and adults; cohort II has replenished the > 50 mg class and, after overwintering and breeding, will die the following summer.

Laboratory-raised individuals do not breed readily at low weights, but field-collected females of 16-17 mg mate and breed successfully at constant temperatures ranging from 15.6° to 26.7°C. Heavier females (> 30 mg), brought in from the field in late winter, invariably breed within a few weeks without having been mated. Their ability to store sperm, observed previously by Heeley (1941), thus permits these individuals to reproduce as soon as warming temperatures induce molting in the field.

Having released their first brood, females undergo a post-parturient molt during which a second marsupium may be developed. The production of second broods appears to be dependent on the weight of the female as well as on temperature: small females tend to breed only once, but increased temperatures induce a higher incidence of second and third broods in individuals of all weight classes. The rest interval between broods ranges from 7 to 17 days, with mean durations of 16.9, 17.2, and 13.4 days at respective temperatures of 15.6°C, 21°C and 26.7°C.

The number of young produced is linearly correlated to female weight, but first broods are significantly larger than second broods even though the animals gain size during the intervening molt. (First brood: $\text{young} = 0.86\ \text{wt} - 6.43;\ r^2 = 0.77$. Second brood: $\text{young} = 0.54\ \text{wt} + 1.97;\ r^2 = 0.50$). Counts of number of progeny released yield estimates of natality, regardless of the total number of eggs carried by the female (fecundity). Occasionally, entire broods consist of non-developing eggs which are eventually expelled by the female; they contribute to what may be termed "egg mortality." Considering only female weight, the 30-50 mg class bred most successfully at all temperatures; as to the effect of temperature, 21°C was most favorable (no more than 10% faulty broods, as compared to up to 20% at 15.6°C and up to 25% at 26.7°C).

In the field two peaks of gravidity are discernible within the yearly breeding period, with 86% and 60% of all potential breeders carrying eggs (percentages based on all females $\geq$ 12 mg). If females with empty marsupia are included, these peaks rise to 93% and 97%, and are no longer as clearly separated. Individuals exceeding 30 mg all become gravid as soon as temperature allows (mid-to late May), and breed a second time. Field evidence also shows that very small females, ($\geq$ 12 mg), are capable of breeding, but become gravid later than heavier individuals. Within the 12-30 mg class, breeding frequency increases gradually through time as juveniles become young reproductive adults during summer growth. Breeding activity in this weight class peaks in late July, about one month after the first reproductive peak of heavier individuals. There are indications that these small females breed only once. But they constitute a large proportion of the gravid females late in the season (older individuals incur heavy mortality losses at that time), and thus contribute significantly to population recruitment, even through each individual may produce only a small number of progeny. By the end of August, no more gravid individuals are found in the field.

The most extensive data on the mortality patterns of *T. rathkei* were gathered by McQueen (1976c) who grew prejuveniles, juveniles and adults at a wide range of temperatures. Our own data were compiled from observations on isolated individuals reared through six weight classes, the limits of which were 0.5-1.34 mg, 1.35-5.0 mg, 12-30 mg, 30-50 mg and 50-80 mg. Comparison between these data and McQueen's (1976c) is difficult because culture conditions and methodology were not identical; but where there is agreement, survivorship trends for the species become apparent.

The most favorable temperature for survival seems to lie around 21°C (both juveniles and adults in McQueen's observations survived best at 20°C). Higher temperatures become increasingly deleterious for all weight classes; at 35°C *T. rathkei* are unable to survive for any significant length of time (McQueen, 1976 c). Temperatures below 20°C also become unfavorable, prejuveniles and juveniles both incurring about 20% mortality at 15.6°C (Table X-2).

If one were to accumulate mortality from the time *T. rathkei* are born until they reach a weight of 50 mg, a little over 28% would have died at 21°C, 38% at 26.7°C, and 54% at 15.6°C. Beyond a weight of 50 mg, mortality increases drastically (Table X-2). The very few females ever collected in the field that exceeded 80 mg indicate that virtually all of these old individuals die before attaining 80 mg.

Females also incur mortality that appear specifically connected to breeding activity. Of 313 females observed through one to three broods, 21 died either during gravidity or during the molt following brood release. The most favorable temperature was again 21°C, and females in the 30-50 mg range survived best during the breeding cycle (Table X-3). At 15.6°C all deaths were linked to non-developing broods. Overall, only 16% of all brooding mortality was due to unsuccessful post-parturient molts.

Table X-2. Percent mortality, within four weight groups, of non-breeding *T. rathkei* females at three constant temperatures.

	Weight Class, mg			
T°C	0.5-5.0	5.01-30.0	30.01-50.0	50.01-80.0
15.6	20.0	19.0	29.4	?
21.0	10.0	8.7	12.1	40.0
26.7	7.0	11.5	14.0	48.9

Table X-3. Percent mortality of *T. rathkei* females associated with each brood within one breeding period (three consecutive broods occurred at 26.7°C only). Assignment to weight classes is based on weights just prior to each brood.

	15.6°C		21°C		26.7°C		
Wt. group	BR. 1	BR. 2	BR. 1	BR. 2	BR. 1	BR. 2	BR. 3
<30	18.2	0.0	0.0	-	0.0	11.1	-
30-50	9.1	8.3	0.0	0.0	3.7	5.6	10.0
>50	18.2	20.0	5.6	10.0	0.0	8.3	0.0

The *Trachelipus rathkei* model

The information discussed above was used to develop and parameterize a model to simulate the population dynamics of *T. rathkei*. The model tracks only females as they pass through seven weight classes, and adjusts their numbers by mortality as environmental conditions dictate. Individuals in sexually mature weight classes pass through breeding stages and produce offspring according to rates determined by their size and by soil temperature. Figure X-1 shows diagramatically the processes affecting individuals of a single weight class.

Passage of individuals through a weight class is modeled as a distributed delay process (see Manetsch, 1976). Each weight class is subdivided into a set of smaller weight ranges, and individuals advance from one subclass (or "bin") to the next at a rate proportional to the growth rate. The distributed delay processes are linked so that individuals leaving the last bin of a weight class enter the first bin of the following weight class.

Growth rate is a function of temperature and is determined by a two-stage degree-day growth model. First, the number of degree-days spent in each weight class, using an appropriate degree-day base temperature, was determined in the laboratory at various temperature, (Table X-1). This information, and daily temperature, are used by the model to calculate the proportion of individuals advancing from each bin during the current time-step, such that mean time spent in a given weight class would allow accumulation of the required number of degree-days at the current temperature. Table X-4 shows the degree-day span and base temperature for each weight class (breeding and non-breeding females were found to have different growth rates, so are modeled separately).

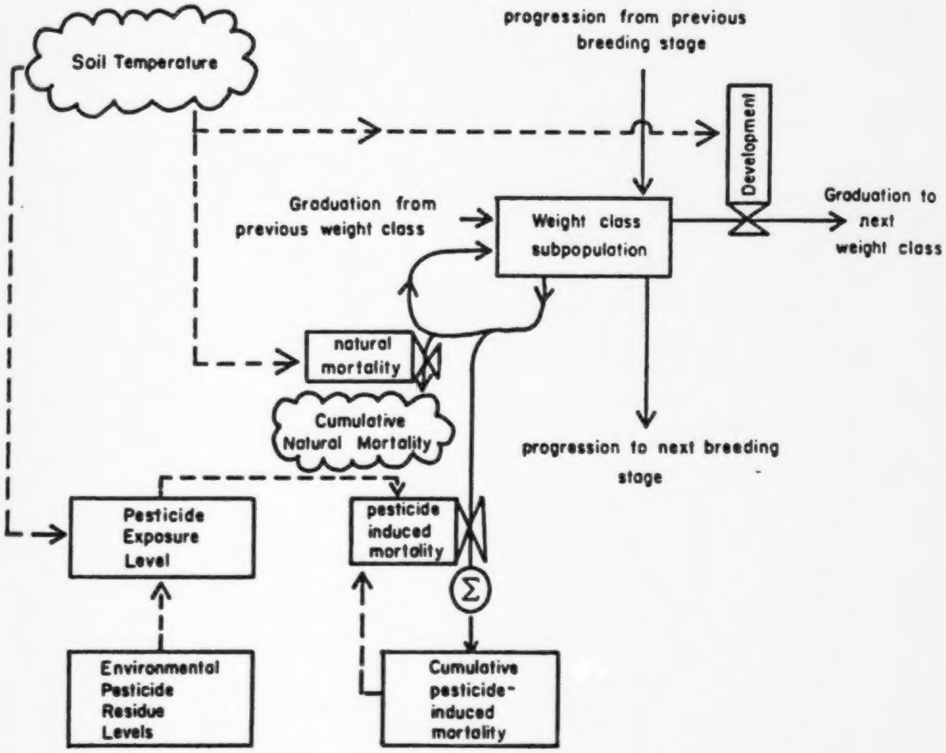

Soil Temperature
progression from previous breeding stage
Development
Graduation from previous weight class
Weight class subpopulation
Graduation to next weight class
natural mortality
Cumulative Natural Mortality
progression to next breeding stage
Pesticide Exposure Level
pesticide induced mortality
Σ
Environmental Pesticide Residue Levels
Cumulative pesticide-induced mortality

Figure X-1. Conceptual model showing processes affecting a life stage of *T. rathkei*. Solid lines represent flow of *T. rathkei*; dashed lines, flow of information. Valves control rate of flow, based on incoming information.

Table X-4. Degree-day-based weight class durations for breeding and non-breeding _T. rathkei_ females.

Weight Class	Base Temperature°C	Degree-Days to Graduate	Order of Distributed Delay
.5-1.34	11°C	319	3 bins
1.35-5.0	11°C	425	4 bins
5-12mg	8°C	432	4 bins
12-30mg (non-breeding)	12°C	560	4 bins
12-30mg (breeding)	9°C	2016	4 bins
30-50mg (non-breeding)	8°C	1303	9 bins
30-50mg (breeding)	7°C	2784	9 bins
50-80mg (non-breeding)	2°C	3147	8 bins
50-80mg (breeding)	4°C	5680	8 bins

Also shown is the number of bins within each weight class (known as the "order" of the distributed delay).

Individuals in sexually mature weight classes (the last four) move not only to bins corresponding to increased weight but also advance through the breeding process (shown as downward movement in Figure X-2). Breeding begins upon accumulation of a specified number of degree-days for each of the last four weight classes. First and second breeding periods are treated as distributed delays, with a mean duration determined from a degree-day model (similar to the one used for advancement through weight bins). Following brood release, breeders enter a fixed-duration rest period (16 days); some will breed again, while others return to the non-breeding population for the remainder of the season.

Figure X-3 shows in greater detail the bins used to track individuals in the population. Movement to the right denotes weight gain, while movement downward (in the mature weight classes) represents progress through the breeding process (other factors suppressed in this figure for clarity). The numbers in each box represent the number of bins down by the number across in that weight class and breeding stage. Thus the position of an individual in Figure X-3 indicates not only its weight, but also its breeding status (carrying first brood, resting after first brood, etc.). Note that a proportion of the individuals completing the first brood return to the top, non-breeding, row without a second brood. Once a given degree-day accumulation is exceeded, no further breeding is initiated.

Graduation from the last vertical bin of a breeding stage is followed by a brood molt, with brood size determined by 2 regression equation. Broods lost to "egg mortality" are subtracted from the egg population at this time.

The only aspect of the model left to be explained is mortality. Three sources of mortality (other than egg mortality) are considered by the model: breeding mortality, pesticide-induced mortality and any other "natural" mortality. Pesticide-induced mortality deserves special treatment and so is covered in a later section. Mortality for breeding females, as displayed in Table X-3 based upon laboratory data, is converted to a table of rates of mortality at three temperatures, and the model interpolates within the

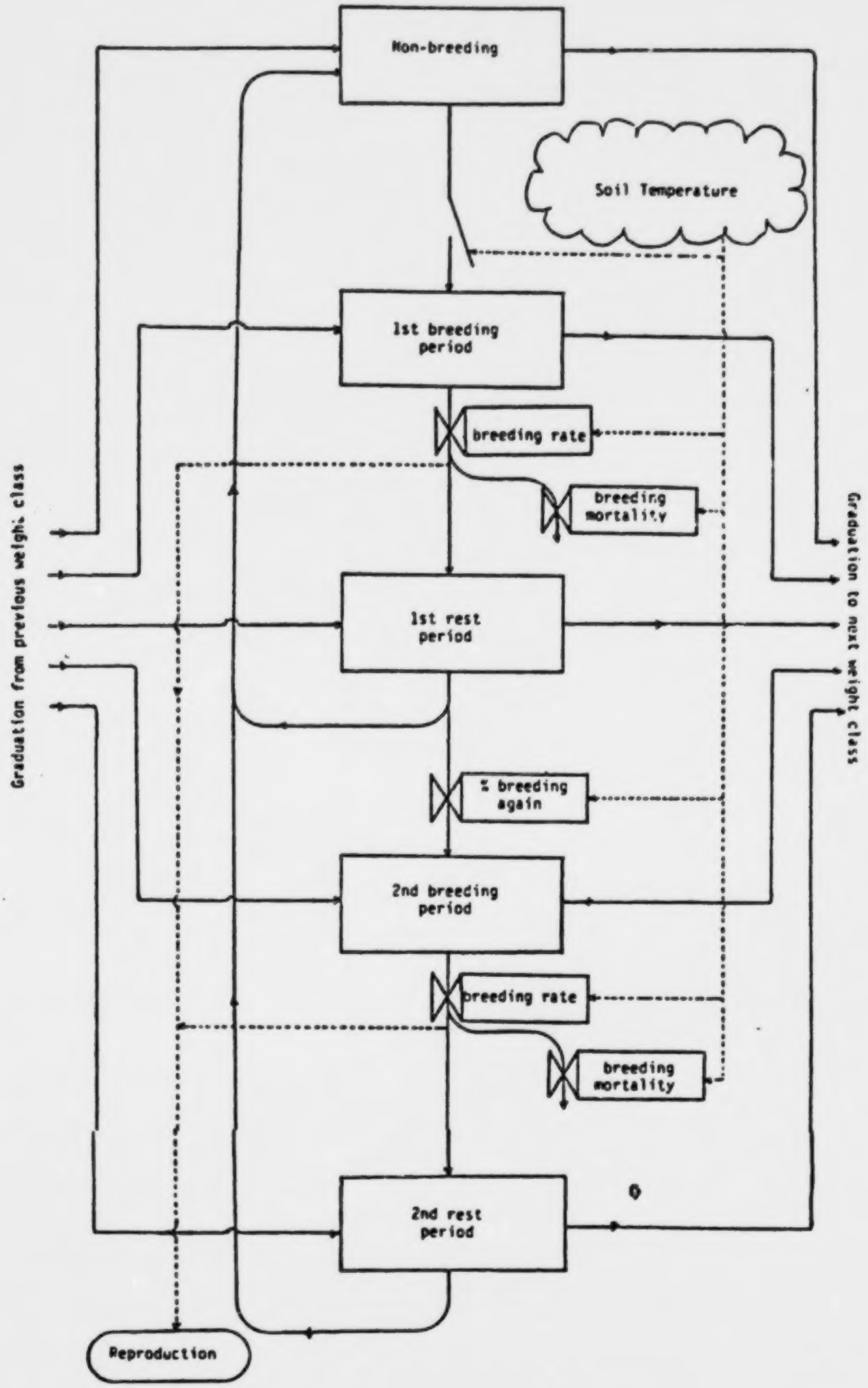

Non-breeding
Soil Temperature
1st breeding period
breeding rate
breeding mortality
1st rest period
% breeding again
2nd breeding period
breeding rate
breeding mortality
2nd rest period
0
Reproduction
Graduation from previous weight class
Graduation to next weight class

Figure X-2. Expanded diagram highlighting the breeding process and the factors affecting it.

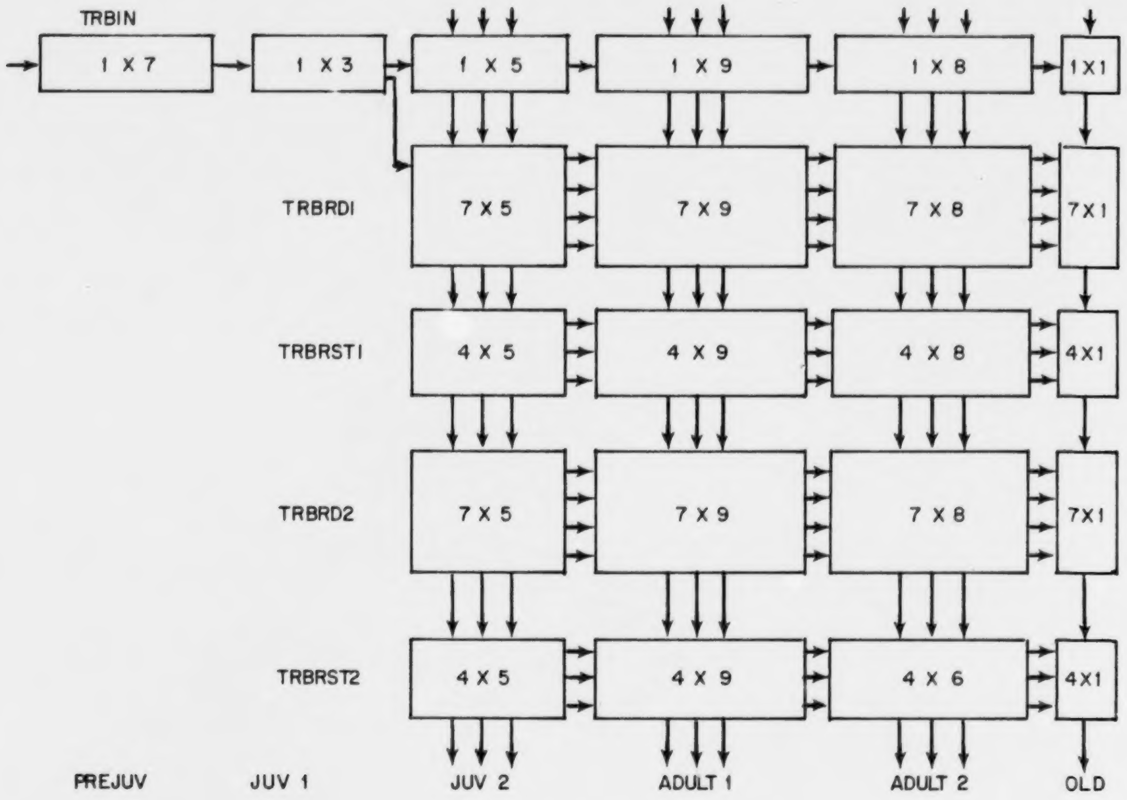

TRBIN
1 X 7
1 X 3
1 X 5
1 X 9
1 X 8
1X1
TRBRDI
7 X 5
7 X 9
7 X 8
7X1
TRBRSTI
4 X 5
4 X 9
4 X 8
4X1
TRBRD2
7 X 5
7 X 9
7 X 8
7X1
TRBRST2
4 X 5
4 X 9
4 X 6
4X1
PREJUV
JUV 1
JUV 2
ADULT 1
ADULT 2
OLD

Figure X-3. Expanded view of the life stages of *T. rathkei* as tracked in the model. Each box indicates the number of bins it contains. Individuals may also leave TRBRST 1 and TRBRST 2 (post-parturient "resting" stages) for the top row of non-breeding classes, although the arrows were omitted to simplify the diagram.

table to determine mortalities at the prevailing temperature as each female completes a brood.

Natural mortality rates determined as a function of temperature under our laboratory conditions (as shown in Table X-2) are not adequate to describe the mortalities observed in the field. That is, if the values in Table X-2 are converted to a table of daily rates at three temperatures, and these values are used to estimate daily rates at other temperatures, the model will allow the population to grow without bound. Some form of density - dependent limitation factor must be introduced in order to allow reasonable dynamics for (unsprayed) populations. Our laboratory and field studies did not identify the limiting processes, but did help to establish approximate upper limits on population densities. However isopod sensitivity to desiccation suggested that availability of suitable moist microhabitat in soil might act as a limiting factor, and a crude model embodying this assumption was developed. This model allows for increased mortalities under dry field conditions, particularly when the population density is high.

The model postulates a typical high density biomass of T. rathkei which can be supported, B_{hi}, and a natural mortality which increases as the total biomass approaches or exceeds that number. The form selected is:

$\text{Mort}_{nat} = \text{mort}_{lab} (1 + 0.10 \times F_{dd})$, where mort_{nat} is (corrected) daily natural mortality, mort_{lab} is the laboratory-based temperature-dependent daily natural mortality, and

$$F_{dd} = \frac{B_{total}}{B_{hi} \cdot F_{moist}}$$

where B_{total} is current total T. rathkei biomass (g/m^2)

B_{hi} is a parameter representing a typical high density of T. rathkei biomass (g/m^2) (currently set at 568 g/m^2), and

$F_{moist} = 1 - (1 + 18 \cdot SM) (e^{-18 \cdot SM})$ where SM is soil moisture (weight/weight) in the top 2 cm of soil.

Several observations should be made about these factors:

(1) with soil moisture $\geq .3$, F_{moist} has little effect, and at low densities, $\text{mort}_{nat} \approx \text{mort}_{lab}$, while at $B_{total} = B_{hi}$, $\text{mort}_{nat} \approx \text{mort}_{lab} \times 1.1$

(2) the soil moisture effect is also weak: with soil moisture at 0.15, mort_{lab} is multiplied by only about 1.13 if $B_{total} = B_{hi}$.

(3) only when B_{total} vastly exceeds B_{hi} and/or soil moisture is extremely low will mort_{nat} be much higher than mort_{lab}, and these conditions, unexplored in the lab, would be expected to have such an effect.

Obviously, these soil moisture - and density-dependent factors have been chosen based only on qualitative observations, and extensive study would be needed before any confidence could be placed in their numerical accuracy. However, they do serve to stabilize the simulated populations and produce reasonable behavior, so they are here adopted in the absence of better information.

Since the male: female ratio of T. rathkei is approximately 1:1 (Snider and Shaddy, 1980), total population at any time is determined by multiplying the female population by a factor of two (recall that the model tracks only females).

AZINPHOSMETHYL TOXICITY

Materials and Methods

T. rathkei were collected in unsprayed areas of the orchard as well as in woodlots around the Michigan State University campus, and were reared in stock cultures for varying periods of time. Very young stages were obtained from isolated gravid females, and the date of their release from the brood pouch was recorded. All cultures were kept at constant temperatures of 15.6°, 21° and 26.7°C, and animals from them were used in experimental runs at these three temperatures. Toxicity tests were arbitrarily terminated after six or seven days, because at that time fungal contamination often began to hinder movement of the animals over the substrate.

Individuals to be tested were selected according to weight, with the exception of second instars which were 2 to 3 days of age. Initially a number of animals were weighed individually and those exceeding the chosen weight limits were rejected. Later on, the good correlation between weight and size, with an r^2 of 0.97 (Snider and Shaddy, 1980) allowed the more rapid technique of selecting individuals by measurement under a dissecting microscope fitted with an ocular micrometer.

In each weight class, and per dosage level, 10 replicate test containers were set up with 2 animals per container (20 animals per test run). The number of times each test run was replicated varied, and will be detailed where needed.

Two different substrates were used for toxicity experiments:

1) Soil collected from unsprayed areas of the orchard: pH 5.5 to 5.7, 3.3 to 3.7 percent organic matter, classified as Marlette silt loam with 22 to 25 percent clay (Pregitzer and Stacey, 1973). It was shaken free from roots, sieved through a 2 mm mesh screen, and dried at 50°C in a vacuum oven.

Azinphosmethyl stock solutions (100 ppm active ingredient) were prepared by adding 100 mg Guthion (50% W.P.) to 500 ml distilled-deionized water. Aliquots of stock in the ratio 5:1 (ml stock: desired ppm in soil) diluted to 100 ml, were used to make up all spiking solutions. Portions of dry soil and 5 ml of the appropriate solution were alternately added to a mixing jar in constant agitation. The final product usually consisted of 200 g soil and 40 ml solution, to yield a moisture content of 20 percent - adequate to ensure survival of *T. rathkei* at all temperatures.

Small portions of prepared soil were then pressed into cylindrical plastic jars (25 mm diameter) such that no cracks were left in which the animals could hide. This allowed observation directly through the clear plastic lid, and major moisture losses could be avoided.

2) Litter: surface litter was raked up in one of the sprayed orchard plots, always in the same general area located in an alleyway between trees. It was chopped into pieces less than 10 mm in length, then mixed and tumbled thoroughly to reduce the effect of patchy pesticide distribution in the field. Litter from control plots, processed in the same way, was used for control runs.

Since all orchard litter was very dry when collected, each batch was brought up to 200 percent moisture based on litter weight. At this moisture level, animals of all sizes survived well. Once moistened, small portions of litter were loosely pressed into plastic jars (25 mm diameter). Two animals were introduced into each jar; the minimum total number of individuals per test run was 20, but depending on availability up to 80 individuals were used per series and weight class.

All litter experiments were run at a constant temperature of 21°C.

Samples of each batch of field litter were set aside at the time the tests were set up, and were analyzed for total azinphosmethyl residues. Unfortunately the sample from one of the collection dates was lost, and pesticide levels had to be estimated by bracketing the missing value with known values from earlier and later dates. Table X-5 gives details of litter collections and analyses.

In experiments with litter, the animals burrowed into the substrate and the smaller sizes especially were difficult to locate without severe disturbance and moisture loss. Therefore only total mortality after a six-day incubation period was recorded; the litter could then be spread out on paper and both live and dead animals could be recovered.

The presence of fecal pellets bore witness to the fact that both soil and litter were ingested during these experiments. Contact and oral toxicity could therefore not be kept apart, but the distinction seems unnecessary if the results are viewed as indications of possible field-effects.

Table X-5. Field-collected litter: results of analyses for total azinphosmethyl residues, and relationship of collection date to the last previous spray application date.

Collection date 1978	July 25	Aug 11	Aug 23	Sept 10
Days since last spray	4	2	14	30
ppm azinphosmethyl	26.7	25.7	11.0*)	3.1

*) By using the ppm values from the two collections bracketing August 23, the missing value was estimated: Degradation rate $x = \sqrt[30]{\frac{3.1}{25.7}}$. Where 30 is the number of days between August 11 and September 10. The unknown concentration $y = (x)^{12}$ (25.7), where 12 is the number of days elapsed since August 11.

RESULTS OF EXPERIMENTS

Soil Toxicity:

Daily records of deaths were kept for use in the *Trachelipus* model, but Table X-6 only gives cumulative percentages per dosage, weight class and temperature, so that an overall view of azinphosmethyl effects might be obtained. (For survivorship on a daily basis see examples given in Table X-7).

An inverse relationship between weight and mortality became clear at all temperatures. While second instars experience up to 37% mortality at 1.0 ppm (26.6°C), animals weighing > 50 mg required dosages in excess of 10 ppm to be appreciably affected (Table X-6). In small animals, the relation between rising temperature and increasing mortality could also be demonstrated. This effect was expected to hold true for all weight classes, but appeared masked by highly variable susceptibility of individual test animals. Given the large number of individuals that needed to be handled to obtain even these few point estimates of azinphosmethyl effects, some sources of error were disregarded. Less variable results could probably have been obtained if exact weights had been used (rather than estimates from size), and if the physiological state of the animals had been more closely monitored. The latter consideration requires observation of feeding activity to exclude those animals which may be fasting prior to an impending molt; and it requires a larger number of replicates so that those that molt during an experimental run can be discarded. Repeated exposure of survivors, as well as monitoring of changing pesticide levels (as a function of time and temperature) would further enhance the accuracy of these experiments.

Table X-6. Cumulative mortality percentages for T. rathkei reared on contaminated soil for 7 days. Data corrected for control by Abbott's formula. *) indicates that the values are means obtained from at least 2 replicate runs (containing 20 animals each).

		AZINPHOSMETHYL, ppm						
T°C	Size class	1.0	2.0	3.0	5.0	10.0	20.0	100
15.6	Instar II	29.9*	6.5*	55.8*	94.8*	94.8	100	
	2-3 mg	0.0		32.9*	0.0	100*		
	15-20 mg				26.3	31.6		
	30-40 mg	5.0				15.0*	26.7	90.0
	50 mg					5.0	20.0*	
21.0	Instar II	20.0*	62.5*	81.7*	86.7*	100		
	2-3 mg	0.0		70.3	16.7			
	15-20 mg				10.0	32.5*		
	30-40 mg				5.0	5.0	100	
	< 50 mg					5.0	5.0	
26.7	Instar II	36.8*	82.1*	94.9*	100*	100*		
	Instar III	12.8		74.4	94.9	100		
	2-3 mg	0.0		38.9	55.6	100		
	5 mg	0.0*		0.0	60.0*	90.0*		
	10 mg	0.0			36.8	100		
	15-20 mg					55.0		
	30-40 mg	3.4*			20.0	7.2*	67.8*	
	50 mg				5.9*	0.0	45.0	

Table X-7. Daily mortality records (cumulated percent) for II. instar *T. rathkei* reared on azinphosmethyl-contaminated soil at three temperatures (20 animals per pesticide level and temp).

T°C	Day after start	1.0	3.0	5.0	10.0	CON
15.6	1	0	0	15	10	0
	2	5	5	35	45	0
	3	5	10	65	70	0
	4	5	10	75	70	0
	5	5	30	80	90	0
	6	5	45	80	90	0
	7	5	55	95	95	0
21.0	1	0	10	15	5	0
	2	0	25	40	35	0
	3	5	40	60	55	0
	4	15	50	85	80	0
	5	20	65	90	90	0
	6	20	75	95	95	0
	7	25	80	95	100	0
26.7	1	0	20	30	45	0
	2	10	55	70	60	0
	3	15	75	85	65	0
	4	15	80	95	100	0
	5	15	90	100		0
	6	20	95			0
	7	25	95			0

Litter Toxicity:

Table X-8 shows mortality percentages for Trachelipus of various weight classes, confined for six days on field-collected litter, at a temperature of 21°C.

The largest size class (mean wt ± S.E. = 62.3 ± 0.98), kept on litter collected 2 days after spraying, experienced greater control than pesticide mortality. Of all weight classes, animals that large have the greatest natural mortality rate (McQueen, 1976c; Snider and Shaddy, 1980); in the field, additional stress due to azinphosmethyl may not have any significant impact on survival. This class was then not further tested; neither were 30-40 mg animals tested after a 5% mortality had been recorded at an estimated level of 11.0 ppm azinphosmethyl.

Within each weight class, the relationship between pesticide level and mortality was quite clear, especially for the highly susceptible small stages. Of particular interest is the fact that second instars still experienced over 50% mortality 14 days after the last spray event in the field, while animals weighing 2 to 3 mg were by that time removed from drastic effects. Even a full month after spraying had ceased, the contaminated litter was still toxic to the smallest prejuveniles.

PESTICIDE EFFECTS MODEL

The fate model described in Chapters I-IV calculates a daily status of pesticide residues in the various orchard compartments. This information is used by models of various orchard-floor-dwelling organisms to calculate the effects of the pesticide exposure on their populations. A new model has been developed which allows estimation of the effects of long-term, rapidly changing exposures on various organisms. This model, and its application to T. rathkei, are discussed next.

General Form

Mortality due to long-term toxicant exposure is a very complex process. Toxicant exposure that might cause 40% mortality in one day will not cause an additional 40% mortality (of either the original population or the survivors) in each subsequent day; nor can the exposure level be expected to remain constant over long time periods. A useful model must calculate new mortality based on both current exposure and past history of exposure (for example, if the genetically most susceptible individuals have already been killed, a new exposure will have less effect). The problem is to capture the most essential aspects of the population's exposure history in a reasonable number of variables for a model to track. The model presented here uses a single, natural, state variable, C_i*, for each size class i, to integrate all of the information about past exposure history that the model will use in calculating further mortality. It is calculated using relatively simple, straightforward assumptions about the temporal response of a population to a toxicant. Figure 3 shows a conceptual model for the effects of the pesticide on a single weight class of the population. (Of course, for a different organism, stratifiction by some characteristic other than weight can be used.)

It should be noted that the laboratory techniques employed (i.e., no use of radiolabeled compounds) did not allow for determination of internal pesticide residues within the isopod population. If such determinations had been

Table X-8. Cumulative percent mortality, over 6 days, of Trachelipus of various weights exposed to field-collected litter contaminated with Guthion (21°C constant temperature). (n = total number of animals per run, distributed as 2 per container).

Days after last spray	Total residue ppm	Weight of test animals (mg)											
		0.5		2-3		15-20		20-30		30-40		> 50	
		Gu	Con	Gu	Con	Gu	Con	Gu	Con	Gu	Con	Gu	Con
4	26.7	93.3	0.0					16.7	2.5				
	n=	60	40					60	40				
2	25.7	100	5.0	80.0	2.5	16.7	0.0			30.0	0.0	6.7	10.0
	n=	80	40	40	40	30	30			20	20	30	20
14	11.0	52.5	5.0	5.0	0.0	5.0	0.0			5.0	0.0		
	n=	80	40	40	20					40	20		
30	3.1	18.3	6.7	6.7	3.3	2.5	0.0						
	n=	60	30	60	30	40	30						

possible, then a model based on a direct relationship between internal pesticide concentration (or concentration in some tissue, for example) and cumulative mortality might have been found, and all of the temporal dynamics could have been included in a compartment-type model for uptake, elimination, and breakdown of the pesticide within the organism (see Goodman, et al. 1977). Instead, the clearly evident lag between initial pesticide exposure (or exposure to increased levels) and the resulting mortality must be represented directly. Examination of the laboratory toxicity results under various conditions shows a general trend of increasing mortality, tapering off as time approaches 7 days. A useful model must at least perform well in calculating the proper total pesticide-induced mortality given an exposure to a constant level of pesticide over a long time period. The rate at which that mortality is expected can be approximated by a fairly simple model, so long as the sum of the daily mortalities approaches the proper cumulative value relatively closely. Thus, a simple expression for incorporating the time dependency has been chosen, illustrated in terms of soil exposure, of the form:

$$c_{i,s}(k) = A\Big(\max\ m_i\big(\mathrm{CONC}(k-1), \mathrm{TEMP}\ (k-1)\big),\ c_{i,s}(k-1)\Big) + (1-A)\ c_{i,s}(k-1), k \geq 1 \quad (1)$$

where : $C_{i,s}(k)$ represents the cumulative mortality, in probits, for the $i^{\underline{th}}$ size class at time (day) k, due only to exposure to pesticide in soil,

CONC(k-1) represents the concentration of pesticide in soil (ppm) at time k-1,

TEMP (k-1) is the estimated soil temperature (°C) at time k-1, at at a depth of 1 cm,

m_i is a function wich specifies the cumulative mortality, in probits, that a population of size-class i would suffer if exposed to CONC (k-1) for many (>>7) days, (i.e., the long-term cumulative mortality under those constant conditions), and

A is a real number in the range $0<A<1$ which specifies the proportion of the "distance" between $C_{i,s}(k-1)$ and $m_i\big(\mathrm{CONC}(k-1), \mathrm{TEMP}\ (k-1)\big)$ that is moved in a single day.

For example, if A = .40, then $C_{i,s}(k)$ will move 40% of the way from $C_{i,s}(k-1)$ to $m_i\big(\mathrm{CONC}(k-1), \mathrm{TEMP}\ (k-1)\big)$ in one day. That is, the cumulative (probit) mortality would increase 40% of the way from its present value to the long-term mortality at the current exposure level, for the size-class i considered. If the concentration and temperature were held constant for many days, then the cumulative mortality $C_{i,s}$ would gradually approach m_i as time continued. Figure X-4 below shows the manner in which $C_{i,s}(k)$ approaches m_i as a fraction of the initial distance between $C_{i,s}(0)$ and m_i, for various choices of A. The variable A could be made size-specific, but was assumed to be a constant in the analysis performed here. Of course, the maximum function in equation (1) is to guarantee that cumulative mortality of the individuals in a given size class never decreases, except as a result of growth into a size class, even though pesticide residue levels may decline.

One significant advantage of this approach for calculating the temporal response to the pesticide lies in its independence from any arbitrarily-defined start or end of periods of exposure. That is, the model does not need to "count up" the days of exposure to a given level of pesticide in order to determine a day's mortality, yet a reasonable mortality rate is obtained daily even when the exposure is long term and changes daily, as with repeated doses and residue attenuation. Of course, this pesticide-induced mortality

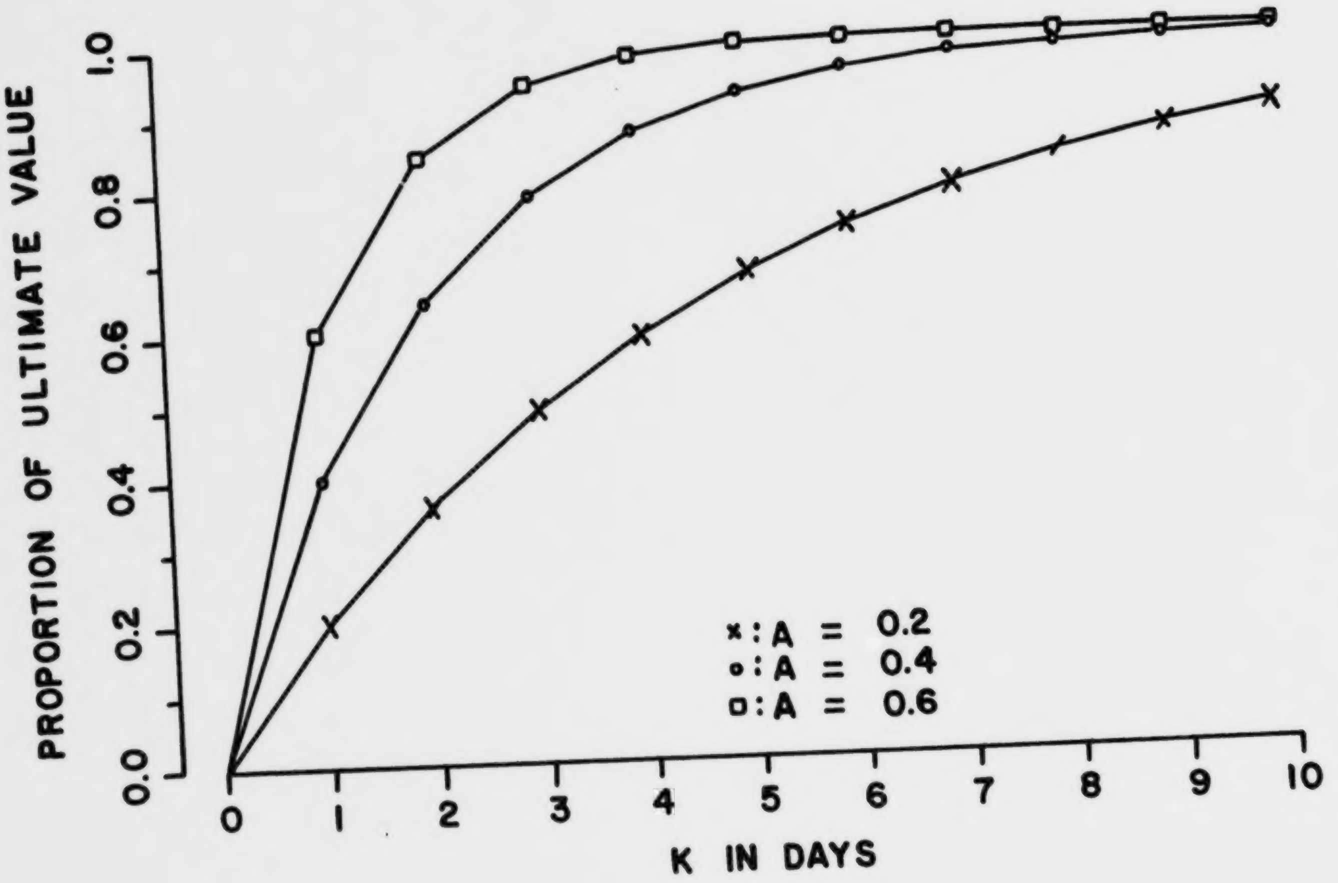


Figure X-4. Time response of $C_{i,s}(k)$. Vertical axis shows the proportion of the distance between $C_{i,s}(0)$ and m_i which $C_{i,s}(k)$ has moved by day k, for various choices of A, the daily change rate.

is independent of any other sources of mortality, which are lumped together as "natural" mortality and extracted daily in another portion of this model, depending on temperature, size class, and breeding condition.

To determine an appropriate value for A and to determine the m_i as functions of pesticide concentration and temperature, an additional modification will be made to the m_i functions in this case: because very few or no lab experiments were run for certain size classes, and because the data are quite noisy, the discrete functions m_i will be replaced by a single function m which depends on size as well as on pesticide concentration and temperature. Once m is fitted, the m_i's are easily calculated by substituting the average size of an individual in the $i^{\underline{th}}$ size class into m. So long as a relatively "smooth" relationship exists between size and susceptibility to the pesticide, a good fit to m_i's can be produced in this manner. (For some organisms or toxicants, the m_i's might be quite different from one lifestage to the next, so separate fits of the m_i's would be mandatory.)

To allow for this size-continuous m function, equation (1) is rewritten as:

$$c_{i,s}(k) = A \cdot \max\Big(m(\text{CONC, TEMP, SIZE}_i), C_{i,s}(k-1)\Big) + (1-A)C_{i,s}(k-1),\ k \geq 1 \quad (2)$$

The use of laboratory data to fit the m function will be described in a later section.

Two other factors must be taken into account in the model. The first involves the lenth of the time steps taken by the model. Each time step (DT) of the model represents .5 day, but equation (2) gives a new cumulative mortality only once per day. The necessary adjustment is to solve for a new variable to replace A (call it B) which will produce a twice-a-day mortality sequence that agrees with the daily sequence at every other step. In more general terms, if DT is any fraction of a day, the appropriate value for B is:

$$B = 1-(1-A)^{DT}, \quad (3)$$

or in our case of $DT = .5$, $B = 1 - \sqrt{1-A}$ (4)

Substituting B into the appropriate places in (2) yields:

$$C_{i,s}(k) = B \cdot \max\Big(m(\text{CONC, TEMP, SIZE}_i), C_{i,s}(k-1)\Big) + (1-B)C_{i,s}(k-1), k \geq 1 \quad (5)$$

where k is now in steps of DT, less than one day.

The final correction is used to adjust for the fact that individuals advance from size class to size class, altering the average cumulative pesticide-induced mortality experienced by a size class. The desired effect is that growt between size classes act like a conservative, dilution-type process operating on the mortalities. The adjustment is performed on the cumulative mortality, not on $C_{i,s}$, its probit. Let $D_{i,s}$ represent the proportion of size class i that has been killed by pesticide in soil before correction for "graduations." That is, $D_{i,s}(k-1) = \text{probit}^{-1}\big(C_{i,s}(k-1)\big)$. Then $D_{i,s}(k-1)$ is adjusted at each time step k by utilizing the number of individuals of size class i-1 advancing to size class i (call this number a_{i-1}), the number advancing from size class i to i+1 (call this a_i), the number alive in size class i at time k-1 (call this $n_i(k-1)$), and the cumulative pesticide-induced mortalities experienced by size classes i-1 and i (denoted $D_{i-1}(k-1)$ and $D_i(k-1)$, respectively). The appropriate cumulative mortality for size class i prior to any new kill at time k is thus:

$$D^*_{i,s}(k-1) = 1 - \frac{n_i \text{ before new pesticide-induced mortality at time } k}{\text{population}_i \text{ if no pesticide-induced mortality existed}}$$

$$= 1 - \frac{n_i(k-1) + a_{i-1} - a_i}{\frac{n_i(k-1)-a_i}{1-D_i(k-1)} + \frac{a_{i-1}}{1-D_{i-1}(k-1)}} \qquad (6)$$

Equation (6) is applied after each time step to adjust the cumulative mortality of each size class, and the resulting $C^*_{i,s}(k-1) = \text{probit}\,(D^*_{i,s}(k-1))$ is the value actually utilized in equation (5) in place of $C_{i,s}(k-1)$.

Assumptions and Implications

The form of the pesticide-induced mortality model introduced above for soil exposure to azinphosmethyl is believed to be applicable to a wide variety of organisms and toxicants. Since this model has not been presented elsewhere, it is perhaps worthwhile to highlight a number of the underlying assumptions and implications of this model:

(i) Toxicant-induced mortality is independent of mortality induced by other (e.g., "natural") causes. Natural mortality occurs in the isopod model as a function of temperature, size, and breeding condition. The toxicant-induced mortality can be "overlaid" on mortality due to predation, climatic extremes, etc.

(ii) It is necessary to track toxicant-induced mortality over long periods of exposure, in the presence of concentrations of toxicant which may be changing with time.

(iii) The model should agree (within the bounds of experimental and statistical fitting errors) with mortalities produced by short- and long-term exposures to constant levels of a toxicant (i.e., laboratory-type situations).

(iv) If the organism is followed through discrete life stages (e.g., size, age, or developmental classes), mortalities should be calculated for each class, adjusting for advancement from class to class.

(v) In the case of a long-term, constant condition exposure to a fixed level of toxicant, a given size class will asymptotically approach but not exceed some level of cumulative mortality. Any subsequent exposure to the same or lower toxicant levels under those conditions will not result in additional mortality (except to individuals which advanced into the size class from a size class with a lower cumulative mortality). This assumption is justified prima facie whenever the mortality is determined by persistent (for example, genetic) differences in the susceptibilities of the individuals in the population. If the differences are due to existence of refuges or similar reasons, and these are not similarly present in the laboratory data used to parameterize the model, then the model may systematically underestimate cumulative mortalities. In this case, an unsatisfying but easily implemented approach to remedying this problem might be to establish an "effective exposure level" for the field situation would be a multiple (>1) of the laboratory exposure, yielding the appropriately higher mortalities upon long-term exposure in the field. Of course, the more desirable alternative is more detailed modeling of the spatial distribution of the pesticide and the organisms.

Combining Mortality Due to Soil, Moss, and Litter Exposure

There are many possible methods for combining estimates of mortalities due to pesticide in soil, moss and litter (or any habitat subdivisions) in the face of exposure that is divided among them: (1) at one extreme, separate $C_{i,s}(k)$, $C_{i,l}(k)$ and $C_{i,m}(k)$ terms could be calculated. Their inverse probit equivalents, $D_{i,s}(k)$, $D_{i,l}(k)$, and $D_{i,m}(k)$ could be combined to get $D_i(k)$ using weightings based on percent activity in each layer. Then the increment in cumulative mortality would be $D_i(k) - D^*_i(k-1)$. This approach in effect subdivides the population into three persistent groups--one in soil, one in litter, and one in moss. While for some types of organisms and habitat divisions this might be appropriate, it is not used here because the organism is highly mobile among the layers. (2) Another method would calculate the $C_{i,s}(k)$, $C_{i,l}(k)$ and $C_{i,m}(k)$ terms based upon $C^*_{i,m}(k-1)$, an activity-weighted average of the $C^*_{i,s}(k-1)$, $C^*_{i,l}(k-1)$, and $C^*_{i,m}(k-1)$. This has the effect of subdividing (by percent activity) the population into three groups, calculating a separate mortality for each, then re-combining them for a new, independent subdivision at the next step. This is the method employed below, and results in the use of a single varialbe $C^*_i(k-1)$ as the pesticide-induced mortality state variable for each size class. That is, the combined $C^*_i(k-1)$ is the only pesticide-induced mortality which is "remembered" for use at time k in equation (5). (3) A further refinement would be to allow individuals to divide their exposures among the three layers at each time step; however, our laboratory studies to not provide any help in parameterizing such a model. It would be very difficult to create an appropriate activity-distribution in the laboratory, so the approximation in (2) was utilized here.

Once $C_i(k)$ and $D_i(k) = \text{probit}^{-1}(C_i(k))$ are calculated, the proportion of the remaining population to be killed at step k is calculated as:

$$\text{KILL}_i(k) = \frac{D_i(k) - D^*_i(k-1)}{(1-D^*_k(k-1))} \qquad (7)$$

Laboratory Parameterization of the Model for Soil Exposure

The search for the m function for this particular organism used multiple regression analysis and began with visual examination of the laboratory-determined 7-day mortalities to seek their relationships with temperature, pesticide concentration, and size-class of the population treated. As is common in toxicity analyses, in which a normal distribution is observed in relating mortality to toxicant exposure variables, the probit transformation was applied to the mortality rates, to provide a more nearly linear response. Because there is no upper or lower limit on the probit variable (i.e., probit (0) = ∞, probit (1.0) = + ∞), artificial upper and lower bounds were introduced. Any mortality below 0.1% was assigned a probit transform value 1.9098, (corresponding to 0.1%), and any mortality above 99.0% was treated as 7.3263 probits. These values were chosen as being close enough to 0 and 100%, respectively, that the difference in model performance would be acceptable, and that unrealistically high probit values would not be generated by the model. Transformations were sought for the size, temperature, and concentration variables to allow a better fit to the dependent (y) variable (cumulative mortality in probits).

Clearly, many of the independent variables interact non-additively in determining the value of the dependent variable. For this organism, long-term pesticide-induced mortality was expected to be related positively to temperature and inversely to size. Further, preliminary analysis suggested that the degree of concentration-dependency was itself size-related. A variety of terms, including the traditional $\log_{10}$ (concentration), were explored in various combinations. A form which did not diverge for CONC = 0 was needed, and the following form for the m function was the best among the forms tried for this organism:

$$m = k_1(\mathrm{TEMP}^{k_2} \cdot (\mathrm{CONC})^{k_3 \cdot \mathrm{SIZE}^{k_r}} \cdot (\mathrm{SIZE})^{k_5} \qquad (8)$$

where m = long term (k>>7) probit cumulative mortality resulting from exposure of organisms of size SIZE (mg) to pesticide at concentration CONC (ppm) at temperature TEMP°C, in our standard laboratory environment (see section X. C. 1)

Equation (8) may not be the best representation for the data, and better fits might be generated if each m_i were fitted separately; however, we wished to test a form which explicitly incorporates the size-dependence of m. In order to ease the problem of fitting this equation a log transformation was done, yielding:

$$\log_{10}m = \log_{10}k_1 + k_2\log_{10}\mathrm{TEMP} + k_3\ \mathrm{SIZE}^{k_4} \cdot \log_{10}\mathrm{CONC} + k_5\log_{10}\mathrm{SIZE} \qquad (9)$$

In this form, a multiple regression analysis could be versus $\log_{10}$TEMP, $\log_{10}$ SIZE, and terms of the form $\mathrm{SIZE}^{k_4}\log_{10}\mathrm{CONC}$, for several choices of k_4, to get a preliminary estimate of the coefficients, for later refinement using the nonlinear optimizing "COMPLEX" procedure of Kuester and Mize (1973). The task remained to estimate the values of m, the dependent variable, from the laboratory measurements of daily cumulative percent mortality observed each day during a 7-day exposure. This required using the parameter A to transform each data point DEAD(k), the probit of observed cumulative mortality on day k, to an estimate of m, the long-term probit mortality for those conditions. The appropriate transformation can be shown to be:

$$m = \frac{\mathrm{DEAD\ (k)}}{1-(1-A)^k} \qquad (10)$$

In this way, better use of the daily mortality data available could be made by including each day's observed cumulative mortality (corrected for control mortality) rather than using only the observations at the end of 7 days. Of course, this approach suffers from the non-independence of the cumulative data taken day after day for the same set of animals, but the departure from the statistical model underlying the analysis was felt to be acceptable in this case, given the nature of the data involved.

The results of the COMPLEX procedure are given by equation (11) below.

$$m = 1.3352\ \frac{\mathrm{TEMP}^{.3339}\mathrm{CONC}^{.2645(\mathrm{SIZE}^{.0363})}}{\mathrm{SIZE}^{.1789}} \qquad (11)$$

The A value which gave the best fit was A = 0.6.

Although the data set is large (1477 observations on groups of 20 animals), the data contain a large amount of noise. It is possible that a better fit would be obtained if each size-class were treated separately. However, there is a large amount of variation evident in the data among replicates of the same conditions, which no model based on temperature, time, concentration and size could explain.

Litter Exposure

The model for mortality in response to litter exposure is identical in form to the model just discussed, and is also based upon a set of laboratory experiments.[7] Because no separate studies for moss exposure were made, the litter exposure model is also applied directly to model moss exposure effects. For the litter experiments, however, the mortality observations were not made daily for 7 days, but rather once, at 6 days. Thus, it was not possible to determine from these data the time course of the mortality, so it is assumed that the A values (determining the rate at which cumulative probit mortality can rise) were identical with those for the soil exposure model. A regression analysis was then performed, with the same set of independent variables as was utilized in the soil toxicity run, but forcing the A value to 0.6, the value selected in the soil regression. All of the litter toxicity laboratory determinations were run at 21°C, so the temperature-dependence term found in the soil toxicity study was normalized and incorporated in the litter equation (12). Finally, the parameters were "fine-tuned" using the COMPLEX procedure as with the soil mortality equation, yielding:

$$C_{i,\text{litter}}(k) = 0.6 \cdot \max\,[C^*_{i,\text{litter}}(k-1),\ m\,(\text{CONC, TEMP, SIZE}_i)] + 0.4\ C^*_{i,\text{litter}}(k-1 \qquad (12)$$

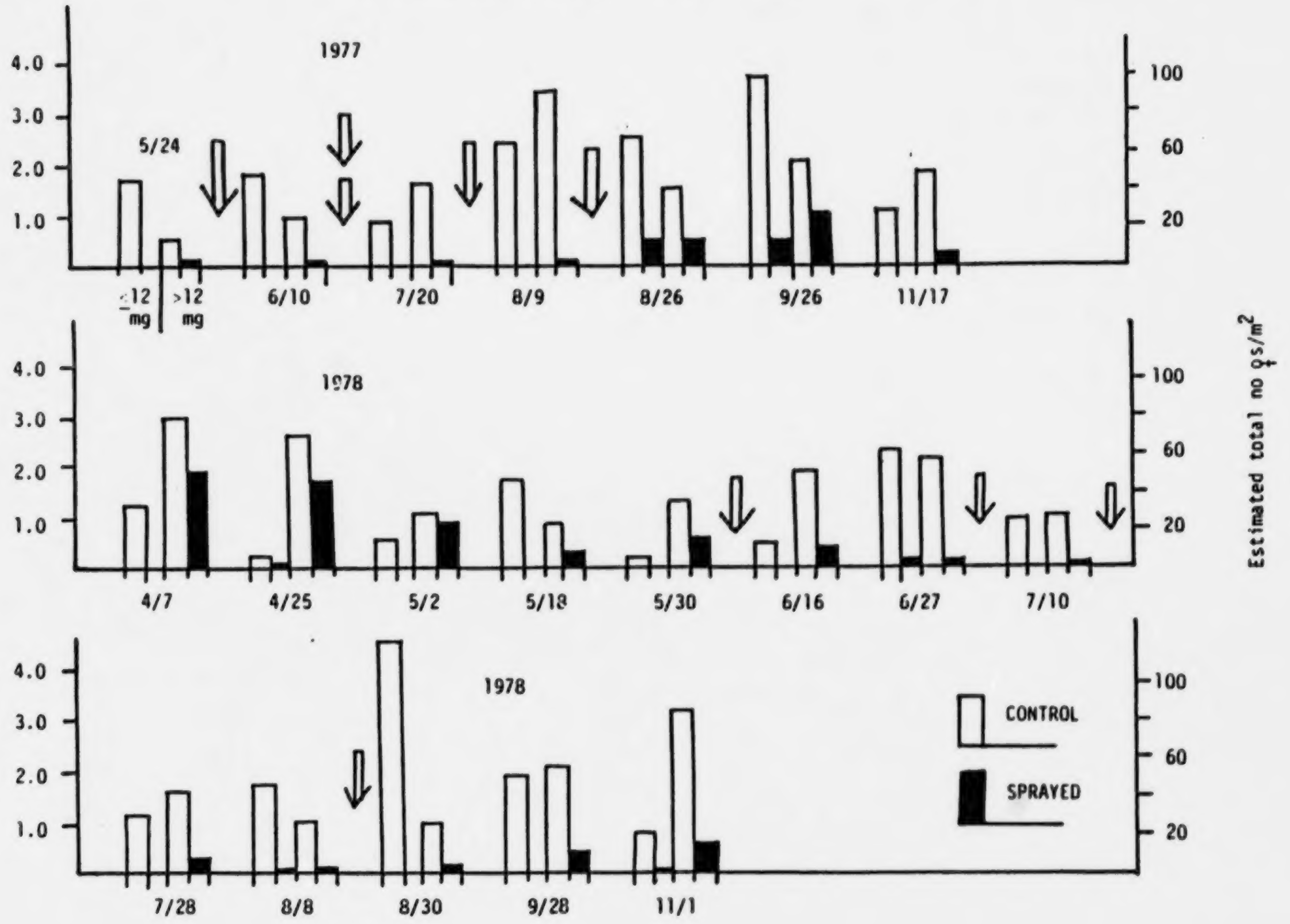
where $m(\text{CONC, TEMP, SIZE}_i) = 3.035 \cdot \text{SIZE}^{-.21} \cdot \text{CONC}^{.33 \cdot \text{SIZE}^{-.18}} \cdot (\frac{\text{TEMP}}{21})^{.33}$

$C_{i,\text{litter}}(k-1)$ is corrected for growth into the size class in the same fashion as equation (6).

Field observation versus predicted mortality under laboratory-based simulation of field conditions

In the same experimental orchard in which the parameters for the pesticide movement and fate model were derived, an extensive program of sampling for T. rathkei was conducted, as reported by Snider.[5] The sampling yielded only a single point estimate of absolute density of isopods, but could furnish an estimate of the relative densities in sprayed versus control plots. Figure X-5 shows the mean numbers of isopods captured per sampling board ($625\ \text{cm}^2$ each), divided into pre-reproductive (42 mg) and reproductive ($\geq$ 12 mg) size classes, in sprayed versus control plots. Table X-9 shows the observed and predicted ratios in sprayed versus control plots on 20 sampling dates in 1977 and 1978. Sprayed plots received 4-5 sprays/year in 1976, 1977, and 1978, at approximately 2 lbs/acre, a typical rate for commercial use. Analysis of the field data shows almost no surviorship of small isopods in the sprayed plots, followed by a nearly 10-fold recovery of the sprayed population prior to the onset of reproduction in the spring, which must therefore be attributed to immigration. The small size of the treatment plots accentuated this effect beyond what would be expected in a commercial orchard. Snider also reported that the size distribution in the sprayed plots was skewed toward the larger sizes, which may be attributable to differential susceptibility to the toxicant, sub-lethal effects on reproduction, and size-related rates of immigration. The reason that the populations in sprayed plots recovered more completely

Figure X-5. Mean numbers of isopods captured/board, in control vs. sprayed plots, broken into size groups of ≤ 12 mg, >12 mg.



in 1978 than in 1977 is not known (see Chapter IX).

Results and Discussion

The pesticide-induced mortality model described above was incorporated into the *T. rathkei* life history model. In order to test the model, a three-year simulation was performed, using as inputs the weather conditions and spray application rates measured in our experimental orchard in 1976, 1977, and 1978. Becasue daily values for the pesticide residue levels in each layer are required for the *T. rathkei* model, the pesticide fate model must be used to estimate these. Thus, the behavior of the *T. rathkei* model is dependent on the validity of the fate model. Figure X-6 shows the simulated *T. rathkei* populations by size class for a control plot, while Figure X-7 represents simulated sprayed plot populations. The model predicted slightly earlier onset of reproduction in 1977 than was seen in the field (see Chapter VIII). The size-dependence of the predicted pesticide-induced mortality is evident in Figure X-7, as is the longer-term effect of this juvenile mortality on adult numbers.

Column 4 of Table X-9 shows the model's predicted ratio of control to sprayed populations. While this measure is designed for comparison with column 3, the (unquantified) size dependency in the sampling efficiency of the field measurements, which employed sampling boards,[5] may have introduced some of the differences between the columns.

Several observations that emerge from examination of Table X-9 appear to be important:

(1) The model predicted very high mortality of small isopods in '78, down to 1.8% of the control populations at the end of the season. Observations in sprayed plots tend to confirm this, with no individuals <12 mg collected on 5 of 8 sampling days after the onset of spraying in 1978. The average of the 8 population observations for <12 mg isopods in the May 31 - November 1,1978 spray season is 1.9% of the control population. As would be expected, the field measurements were much more variable than the model predictions, but they are in good general agreement. In both 1977 and 1978, the predicted mortality for small isopods was not as high as was observed in the field, which makes it even more interesting that adult populations were actually higher than predicted in sprayed plots. These observations indicate that in some way, the adult populations in sprayed plots are recovering, both within and between seasons. For example, the sprayed plot adult populations captured went from 2.9% of controls to 33.3% of controls between August 9 and August 26, 1978, while not a single surviving small isopod was captured in a sprayed plot that season. This points toward either a large amount of immigration of adults into the (rather small) sprayed plots, or a sampling bias (e.g., the possibility that post-spray sampling did not collect surviving adults proportionally to their numbers, due to immobilization by pesticide. This is considered by the authors to be unlikely). In a sprayed plot large enough to reduce the effects of immigration, the populations are unlikely to display the behavior shown in Table X-9. The model prediction of adult sprayed plot population (last column) increase from 08.4% to 13.3% of control populations during the over-wintering period is explained by the slight density-dependence of natural mortality in the model.

The model may not predict high enough mortality of <12 mg isopods. This may reflect on the transformation of laboratory pesticide exposures in ppm into field units of $\mu g/cm^2$, a process which obviously depends not only on the pesticide profile in the orchard layers, but also on the isopod's behavior.

CONCLUSIONS

Further work, some of which has already been undertaken, will be necessary before better tests of the general model presented here can be made. Several difficulties are evident to the authors:

(1) Immigration was very significant in the small experimental plots, but is not represented in the model, which simulates a closed population. This is not a flaw in the mortality model, but a factor which affects its comparison to the field data.

(2) The process of converting from the fate model's estimate of $\mu g/cm^2$ pesticide in soil to the ppm required in the *T. rathkei* model needs further refinement. This is a classical problem--to relate lab determinations to field measurements. It is confounded with the need to estimate the depth of soil residues to which the organism is exposed.

(3) The distribution of the organism's activity between soil and other layers is not well established.

(4) Possible effects of the pesticide on fecundity are not incorporated in the present model. However, the much higher sensitivity of smaller size classes to the pesticide may make the simplification acceptable for this organism, since it makes little difference whether the females subjected to sublethal pesticide levels do not produce viable off-spring or whether the offspring die shortly after birth due to direct exposure.

(5) The noisy laboratory data for *T. rathkei* and the attendant difficulty in deriving parameters for the m function from them mask the performance of the general model form developed here.

More work is needed to determine a variety of good forms for m functions, since various organisms (and life stages) and toxicants may behave quite differently. It would be useful to have a library of forms which could be selected among for parameterizing a model of a particular organism and toxicant.

A model of this form can be useful even if it is not yet sufficiently validated to allow direct use of its predicitons for a particular population. If the model represents the current understanding, based on laboratory studies, of the effects of a toxicant on a population, and if its predictions do not agree with field measurements, the model is an excellent tool for discovering the discrepancies and exploring the possible explanations for the discrepancies.

In order to simulate the effects of a toxicant on an ecosystem, for integrated pest management or other purposes, a model must not only incorporate single-species population components, but also represent their interactions with each other and with the environment. However, models which represent the direct effects of long-term, time-varying exposures of populations to a toxicant remain as important steps toward the goal of relating the behavior of toxicants in the laboratory to their effects in the environment.

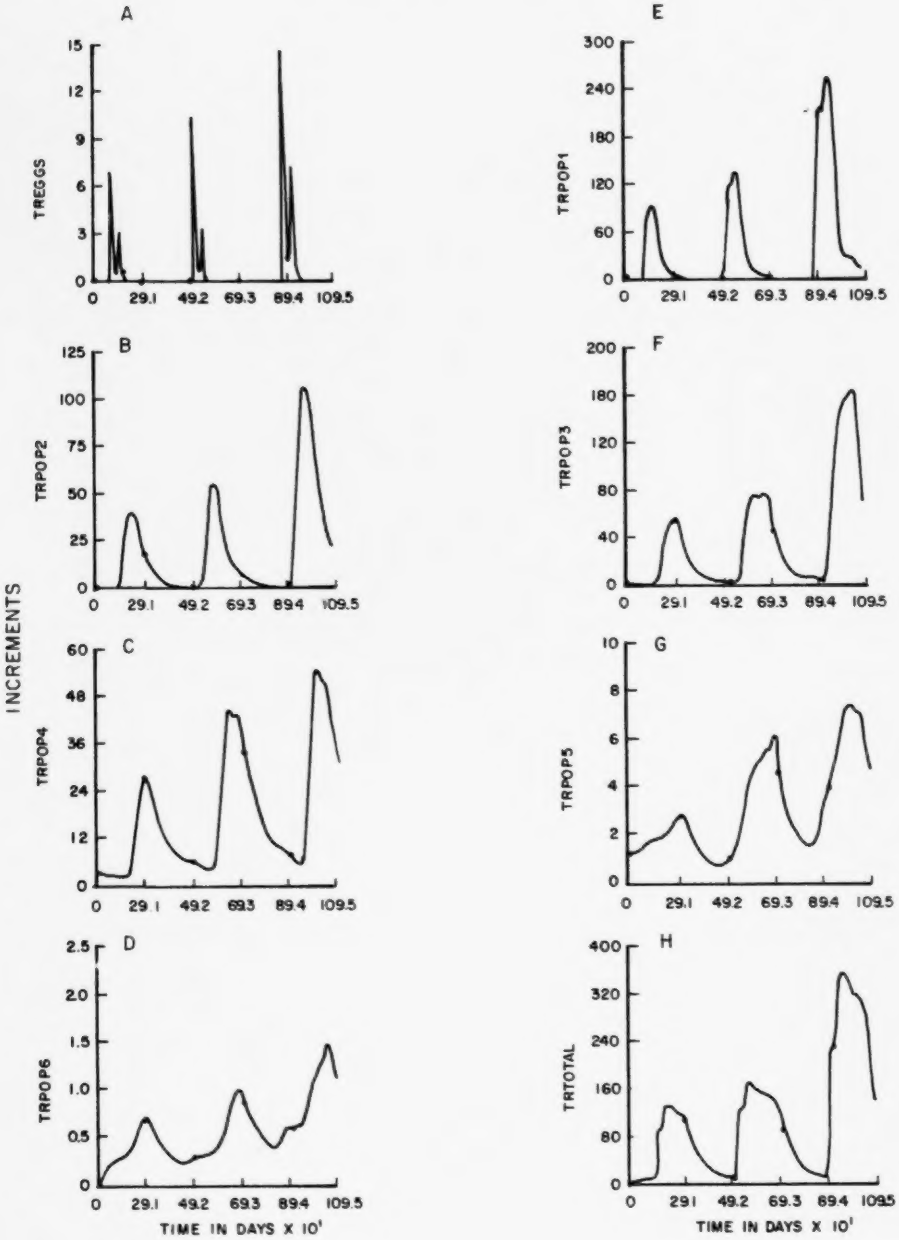


Figure X-6. Simulated populations (number/m^2) of *T. rathkei* for three years in a control (unsprayed) plot: (a) eggs (daily hatch), (b) 0.5-5 mg, (c) 5-12 mg, (d) 12-30 mg, (e) 30-50 mg, (f) 50-80 mg, (g) >80 mg, (h) totals, excluding eggs.

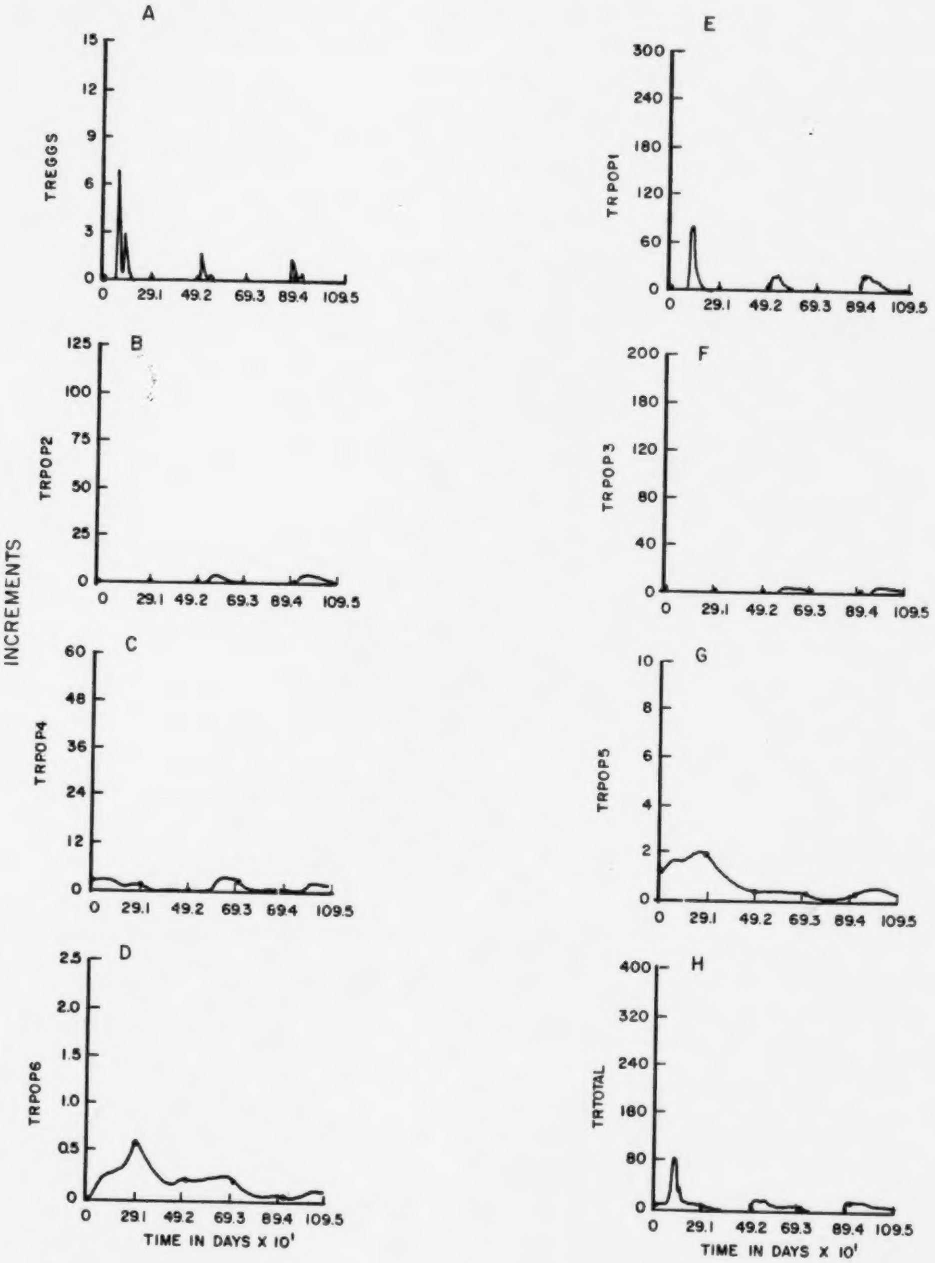


Figure X-7. Simulated populations (number/m^2) of *T. rathkei* for three years in a plot sprayed with azinphosmethyl (see Pesticide Fate Model section): (a) eggs (daily hatch), (b) 0.5-5 mg, (c) 5-12 mg, (d) 12-30 mg, (e) 30-50 mg, (f) 50-80 mg, (g) >80 mg, (h) totals, excluding eggs.

Table X-9. Comparison of field data with model predictions. Columns 3 and 4 are the ratios of numbers of pre-reproductive (<12 mg) and reproductive (≥12 mg) *T. rathkei* collected per sampling board from control plots to number per board from sprayed plots, for each sampling day.[5] Last two columns are the model's prediction, given the environmental and pesticide application inputs observed in the field, of the ratios of <12 mg and ≥ 12 mg populations from unsprayed and sprayed plots on the same day.

SPRAY/CONTROL RATIOS

		Observed		Predicted	
Date	Day of Model Run	<12 mg	> 12 mg	<12 mg	>12 mg
1977					
May 24	509	0.0	0.200	0.429	0.343
June 10	526	0.0	0.107	0.230	0.337
July 20	566	0.0	0.32	0.061	0.205
Aug 9	586	0.0	0.029	0.049	0.124
Aug 26	603	0.010	0.333	0.041	0.102
Sept 26	635	0.009	0.525	0.035	0.083
Nov 17	686	0.0	0.118	0.037	0.084
1978					
Apr 7	827	0.0	0.633	0.259	0.133
Apr 25	845	0.218	0.648	0.056	0.133
May 2	852	0.0	0.825	0.051	0.132
May 18	868	0.0	0.381	0.063	0.131
May 30	880	0.0	0.451	0.063	0.130
June 16	897	0.0	0.252	0.103	0.128
June 27	908	0.091	0.064	0.125	0.127
July 10	921	0.0	0.056	0.045	0.126
July 28	939	0.0	0.210	0.024	0.107
Aug 8	950	0.009	0.084	0.038	0.086
Aug 30	972	0.0	0.182	0.022	0.055
Sept 28	1001	0.0	0.220	0.018	0.041
Nov 1	1035	0.053	0.196	0.018	0.040

Definitions of Symbols in Chapter X

A	Proportion of distance between $C_i(k-1)$ and m_i $\left(\text{CONC}(k-1),\ \text{TEMP}(k-1)\right)$ that is moved in one day; i.e., fraction by which mortality (in probits) can change from its current to its ultimate value under given conditions in one day.
$a_{i-1}(k)$	Number/m^2 of individuals "graduating" from size class i-1 into size class i at time k.
$a_i(k)$	Number /m^2 of individuals "graduating" from size class i into size class i into size class i+1 at time k.
B	Analogous to A, but corrected for time steps of durations less than one day.
$C_i(k)$	Cumulative mortality, in probits, for the $i^{\underline{th}}$ size class at time k, due only to pesticide exposure, before correction for growth of individuals into and out from the size class†.
$C_i^*(k)$	Corrected cumulative mortality, in probis, for the $i^{\underline{th}}$ size class at time k, due only to pesticide exposure. Mathematically defined as probit $\left(D_i^*(k)\right)$. †
CONC(k)	Concentration of pesticide in a layer (litter, moss, or soil) in parts per million (ppm) at time k.
$D_i(k)$	Proportion (not in probits) cumulative mortality for size class i due to pesticide, before correction for mortalites of new "graduates" into the size class†. Mathematically, $D_i(k) = \text{probit}^{-1}\left(C_i(k)\right)$.
$D_i^*(k)$	Proportion (not in probits) cumualtive mortality for size class i due to pesticide, after correction for mortalities of new "graduates" into the size class using equaiton (10)†.
DEAD(k)	Laboratory-observed cumulative pesticide-induced mortality on day k of a 7-day experiment, after correction for mortality of control population.
k	Index of time step in the model. Length of time step can vary, but is commonly 1 day or 0.5 day.
$\text{KILL}_i(k)$	New pesticide-induced mortality (a proportion, not a probit) for size class i on day k due to pesticide exposure.
k_1, k_2, k_3, j_4, k_5	Coefficients in mortality function, equation (2).
m	$\equiv$ m(CONC, TEMP, SIZE). Long-term cumulative mortality under constant exposure with a given CONC, TEMP, and SIZE. Fitted using data for all size classes, as a continuous function of size.
m_i	$\equiv m_i$(CONC, TEMP). Long-term cumulative mortality for size class i under constant exposure with a given CONC, TEMP.†

$n_i(k-1)$	Number/m^2 of individuals alive in size class i at time k-1.
SIZE	Weight (mg) of an organism.
SIZE$_i$	Parameter representing average weight (mg) of organisms in the i^{th} size class.
TEMP(k)	Estimated mean soil temperature (°C) for time step k at depth of 1 cm. For laboratory data, TEMP represents the temperature at which the environment was maintained during the pesticide exposure of the organisms.

† Additional subscripts l, m or s specify that mortality is due only to pesticide exposure in litter, moss, or soil layers, respectively.

REFERENCES

Al-Adil, K. M., E. R. White, W. L. Winterlin, and W. W. Kilgore. 1973. Uptake and Translocation of Guthion by Beans and Barley. J. Agric. Food Chem. 21:376-379.

Aritajat, U., D. S. Madge and P. T. Gooderham. 1977. The effects of compaction of agricultural soils on soil fauna. I. Field investigations. Pedobiol. 17:262-282

Armstrong, D. E. and J. G. Konrad. 1974. Nonbiological degradation of pesticides. In Pesticides in Soil and Water. (Ed. by W. D. Guenzi). pp. 123-131. SSSA. Madison, WI.

Asmussen, L. E., A. W. White, Jr., E. U. Hauser, and J. M. Sheridan. 1977. Reduction of 2,4-D load in surface runoff down a grassed waterway. J. Environ. Qual. 6:159.

Bakker, K., 1956. Feeding activity patterns in *Porcellio scaber* LATR. Proc. K. Ned. Akad. Wet. Ser. C, 59-750-757.

Barley, K. P. 1958. Earthworms and soil fertility. I. Earthworm populations found in agricultural land near Adelaide. Aust. J. Agr. Res. 10:171-178.

Barrow, G. M. (1966) Physical Chemistry. McGraw-Hill, Inc., New York. 843 pp.

Bauer, J. R., Bovey, R. W. and Merkle, M. G. (1972) Concentration of Picloram in runoff water. Weed Sci. 20, 309-314.

Behrens, W. V. 1929. Ein Beitrag zur Fehlerberechnung bei wenigen Beobachtungen. Landwirtsch. Jahrb. 68:807-837.

Beynon, K. I., Davies, L., and Elgor, K. (1966) Analysis of crops and soils for residues of diethyl 1-(2,4 dichlorophenyl)-2-chlorovinyl phosphate. J. Sci. Food Agr. 17, 167-174.

Bouché, M. B. 1972. Lombriciens de France. Ecologie et systématique. Ed. I.N.R.A., Annales de Zoologie, numero special 72.2, 1-671.

Brereton, J. LeG., 1956. The distribution of woodland isopods. Oikos 8:85-106.

Brown, A. W. A. (1978) Ecology of Pesticides. John Wiley and Sons, New York, 525 p.

Brown, A. W. A. (1977) How have entomologists dealt with resistance. Proc. 68th Ann. Meet. Am. Phytopathol. Soc. 3, 67-74.

Bridges, R. C. and Farrington, J. A. (1974) A compartmental omputer model of foliar uptake of pesticides. Pestic. Sci. 5, 365-381.

Bukovac, M. J. (1976) Herbicide entry into plants. In Herbicides:Physiology, Biochemistry, Ecology. (Ed. by Audus, L. J.), pp. 335-364. Academic Press, London.

Carnio, J. S. 1974. A laboratory study on the effects of some climatic factors on the demography of the terrestrial isopods, *Porcellio spinicornis* Say and *Tracheoniscus rathkei* Brandt. M. Sc. Thesis, York University, Toronto, Ontario.

Caro, J. H., Taylor, A. W. and Lemon, E. R. (1971) Measurement of pesticide concentrations in air overlying a treated field. International Symposium on Identification and Measurement of Environmental Pollutants, Ottawa, Canada.

Caro, J. W., Freeman, H. P., and Turner, B. C. (1974) Persistence in soil and losses in runoff of soil-incorporated carbaryl in a small watershed. J. Agric. Food Chem. 22, 860.

Chapell, H. G., T. F. Ainsworth, R. Cameron and M. Redfern. 1971. The effect of trampling on a chalk grassland ecosystem. J. Appl. Ecol. 8:869-882.

Claith, M. M., Spencer, W. F., Farmer, W. J., Shoup, T. D., and Grover, R. (1980) Volatilization of S-ethyl n,n-dipropylthiocarbamate from water and wet soil during and after food irrigation of an alfalfa field. J. Agric. Food Chem.. 28, 610-613.

Cox, G. W. (1974) Laboratory Manual of General Ecology. Wm. C. Brown Company, Dubuque, Iowa, 196 p.

Croft, B. A. (1975) Tree fruit pest management. In Introduction to Pest Management. (Eds. Metcalf, R. L. and Luckmann, W. H.). Wiley Interscience, New York.

Croft, B. A. (1978) Potentials for research and implementation of integrated pest management on deciduous fruit-trees. In Pest Control Strategies (Eds. Smith, E. H. and Pimentel, David), p. 101-115. Academic Press, New York.

Croft, B. A. and Brown, A. W. A. (1975) Responces of arthropod natural enemies to insecticides. Ann. Rev. Entomol. 20, 285-335.

Crosby, D. G. (1969) Experimental approaches to pesticide photodecomposition. Residue Reviews 25, 1-12.

Crosby, D. G. (1970) The non-biological degradation of pesticides in soils. In Pesticides in the Soil: Ecology, Degradation, and Movement, p. 86-94, Mich. State Univ., East Lansing, MI.

Crosby, D. G. (1973) The fate of pesticides in the environment. Ann. Rev. Plant Physiol. 24, 467.

Day, B. E., Jordon, L. J. and Hendrixson, R. T. (1961) The decomposition of amitrole in California soils. Weeds 9, 443-456.

DeJong, K. (1980) Adaptive system design: a genetic approach. IEEE Trans. Syst. Man Cybern., SMC-10, p. 566-574.

Duffey, E. 1975. The effects of human trampling on the fauna of grassland litter. Biol. Conserv. 7:255-274.

Eason, R. and W. H. Whitcomb. 1965. Life history of the dotted wolf spider Lycosa punctulata Hentz (Araneida: Lycosidae). Arkansas Acad. Sci. Proc. 19:11-20.

Ebling, W. 1963. Analysis of the basic processes involved in the deposition, degradation, persistence and effectiveness of pesticides. Residue Reviews 3, 35.

Edgar, W. D. 1970. Prey and feeding behavior of adult females of the wolf spider Parodsa parmentata. Netherl. J. Zool. 20:487-491.

Edgar, W. D. 1971. The life cycle, abundance and seasonal movement of the wolf spider, Lycosa (Pardosa) lugubris, in Central Scotland. J. Anim. Ecol. 40:303-322.

Elliot, D. L., Iwata, Y., Carman, G. E., and Gunther, F. A. 1977. Post-application slough-off of pesticide deposits on orange trees. Bull. Environ. Contam. Toxicol. 18, 711-718.

Eto, M. (1974) Organophosphate pesticides: organic and biological chemistry. CRC Press, Cleveland, Ohio. 368 p.

Evans, A. C. and W. J. McL. Guild. 1948. Studies on the relationships between earthworms and soil fertility. IV. On the life cycles of some British Lumbricidae. Ann. Appl. Biol. 35:471-484.

Faust, S. D. and Gomaa, H. M. 1972. Chemical hydrolysis of some organic phosphorus and carbamate pesticides in aquatic environments. Environ. Lett. 3, 171-201.

Felsot, A. and Dahm, P. A. (1979) Sorption of organophosphorus and carbamate insecticides by soil. J. Agric. Food Chem. 27, 557-563.

Freed, V. H., Chiou, C. T. and Schmedding, D. W. 1979. Degradation of selected organophosphate pesticides in water and soil. J. Agric. Food Chem. 27, 706-708.

Geiser, S. W. 1934. Further observations on the sex-ratios of terrestrial isopods. Field & Lab. 3:7-10.

Gillette, J. W. and Witt, J. M., Eds. (1979) Terrestrial Microscosms Proc. Symp. Workshop on Terrestrial Microscosm, NSF/RA 790034.

Glass, B. L.. and Edwards, W. M. (1974) Picloram in lysimeter runoff and percolation water. Bull. Environ. Contam. Toxicol. 11, 109-112.

Glass, E. H. and Lienk, S. E. (1971) Apple insect and mite populations developing after discontinuance of insecticides: 10 year record. J. Econ. Entomol. 63/23-26.

Goodman, E. D. 1982. Modeling effects of pesticides on populations of soil/ litter invertebrates in an orchard ecosystem. Env. Toxicol. and Chem. 1, 45-60.

Goodman, E. D. 1977. Ecosystem responses to alternative pesticides in the environment: A systems approach. Final Report, EPA Project No. R-803859, Corvallis, OR. pp. 230-253.

Goring, C. A. I., Laskowski, D. A., Hamaker, J. W. and Meikle, R. W. (1975) Principles of pesticide degradation in soil. In Environmental Dynamics of Pesticides (Eds. Haque, R. and Freed, V. H.), p. 135-172. Plenum Press, New York.

Grégoire-Wibo, C. 1975. Bioécologie et dynamique de population de Collemboles. Ph.D. Thesis, Université Catholique de Louvain, Fac. des Sciences, 1-217.

Grubbs, F. E. (1969) Procedures for detecting outlying observations in samples. Technometrics 11, 1.

Gunther, F. A. 1969. Insecticide residues in California citrus fruit and products. Residue Reviews 28.

Gunter, F. A. and Blinn, R. C. (1955) Analysis of Insecticides and Acaricides. Interscience, New York.

Gunther, F. A., Westlake, W. E., Barkley, J. H., Winterlin, W. and Langbehn, L. 1973. Establishing dislodgeable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 9, 243-249.

Gunther, F. A., Iwata, Y., Carman, G. E., and Smith, C. A. 1977. The citrus reentry problem: research on its causes and effects, and approaches to its minimization. Residue Reviews 67, 1-139.

Hall, A. S. and Day, J. W., Jr., Eds. (1977) Ecosystem Modeling - In Theory and Practice. Wiley-Interscience, New York. 684 p.

Hall, F. R., Reichard, D. L., and Krueger, H. R. (1975) Dislodgeable azinphosmethyl residues from air blast spraying of apple foliage in Ohio. Arch. Environ. Contam. Toxicol. 3, 352-363.

Hall, J. K., Paulus, M. and Higgins, E. R. (1972) Losses of atrazine in runoff water and soil sediment. J. Environ. Quality 1, 172-176.

Hamaker, J. W. (1972) Decomposition: quantitative aspects. In Organic Chemicals in the Soil Environment. (Eds. Goring, C. A. I. and Hamaker, J. W), p. 253-340. Marcel Dekker, New York.

Hansen, J. D., Schneider, B. A., Olive, B. M., and Bates, J. J. (1978) Personnel safety and foliage residue in an orchard spray program using azinphosmethyl and captan. Arch. Environ. Contam. Toxicol. 7, 63-71.

Harris, C. R. 1967. Further studies on the influence of soil moisture on the toxicity of insecticides in soil. J. Econ. Entom. 60:41-44.

Harris, C. R. 1970. Laboratory evaluation of candidate materials as potential soil insecticides. III. J. Econ. Entom. 63:782-787.

Harris, C. R. 1971. Influence of temperature on the bilogical activity of insecticides in soil. J. Econ. Ent. 64 (5): 1044-1049

Harrold, L. L., Triplet, G. B., Jr., and Edwards, W. M. (1970) No-tillage corn-characteristics of the system. Agric. Eng. 51, 128.

Hartley, G. S. (1969) Evaporation of pesticides. In Pesticide Formulations Research. (Ed. Gould, R. F), p. 115-134. Am. Chem. Cos. 'Advances in Chemistry Series,' 86.

Hatchett, S. P. 1947. Biology of the Isopoda of Michigan. Ecol. Monogr. 17:48-79.

Haynes, R. J. (1980) Influence of soil management practice on the soil agro-ecosystem. Agro-Ecosystems 6, 3-32.

Heeley, W. 1941. Observations on the life histories of some terrestrial isopods. Proc. Zool. Soc. London, B, III:79-149.

Helling, C. S., Kearney, P. C., Alexander, M. (1971) Behavior of pesticides in soils, Adv. Agron. 23, 147-241.

Hill, K. R. (1971) Report of half-life working party. J. Ass. Offic. Anal. Chemists 54, 1316-1317.

Holland, J. H. (1975) Adaptation in natural and artificial Systems. The University of Michigan Press, Ann Arbor. 183 p.

Howitt, A. T. and Pshea, A. (1965) The development and use of ultra low volume ground sprayers for pests attaching fruit. Mich. Quart. Bull. 48:144-160.

Hoyt, S. C. and Burts, E. C. (1974) Integrated control of fruit pests. Ann. Rev. Entomol. 19, 231-252.

Hull, H. G. (1970) Leaf structure as related to absorption of pesticide and other compounds. Residue Reviews 31, 1-150.

Iwata, Y., Ousch, M. E., Westlake, W. E., and Gunther, F. A. 1975. Behavior of five organophosphorus pesticides in dust/derived from several soil types. Bull. Environ. Contam. Toxicol. 14, 49.

Iwata, Y., Westlake, W. E., Barkley, J. H., Carman, G. E., and Gunther, F. A. (1977) Behavior of phentohoate (cidial) deposits and residues on and in grapefruits, lemons and lemon leaves, oranges and orange leaves, and in the soil beneath orange trees. J. Agric. Food Chem. 25, 362-368.

Kadoum, A. M. (1967) A rapid micromethod of sample cleanup for gas chromatographic analysis of insecticidal residues in plant, animal, soil, and surface and ground water extracts. Bull. Environ. Contam. Toxicol. 2, 264.

Katan, J., Fuhrmann, T. W. and Lichtenstein, E. P. (1976) Binding of ^{14}C parathion in soil: a reassessment of pesticide persistence. Science 193, 891-894.

Kaufman, D. D. (1964) Microbial degradation of 2,2-dichloro-propionic acid in five soils. Can. J. Microbiol. 10, 843-852.

Kearney, P. C. and Helling, C. S. (1969) Reactions of pesticides in soils. Residue Reviews 25, 25-44.

Khan, M. A. Q., H. M. Khan and D. J. Sutherland. 1974. Ecological and health effects of the photolysis of insecticides. In *Survival in Toxic Environments*, M. A. Q. Khan and J. P. Bederka, eds. Academic Press. pp. 333-355.

Khan, M. A. Q., Khan, H. M., and Southerland, D. J. (1976) Ecological and health effects of the photolysis of insecticides. In Survival in Toxic Environments (Eds. Khan, M. A. Q. and Bederka, J. Pl, Jr.), p. 333-355. Academic Press, New York.

Klingman, G. C. and Ashton, F. M. (1975) Weed Science: Principles and Practices. Wiley Interscience, New York, p. 32-33.

Kuester, J. L. and J. H. Mize. 1973. *Optimization Techniques with FORTRAN*. McGraw-Hill.

Kuhr, R. J., Davis, A. C. and Bourke, J. B. (1974) Dissipation of Guthion, Sevin, Polyram, Phygon and Systox from apple orchard soil. Bull. Environ. Contam. Toxicol. 11, 224-230.

Lassiter, R. R., Baughman, G. L. and Burns, L. A. 1978. Fate of toxic organic substances in the aquatic environment. In State-of-the-Art in Ecological Modeling (Ed. S. E. Jorgensen). pp. 219-245. Inter. Soc. Ecol. Mod., Copenhagen.

Leonard, R. A., Bailey, G. W., Swank, R. R., Jr. (1976) Transport, detoxification, fate and effects of pesticides in soil and water environments. In Land Application of Waste Materials, 49-78. Soil Conservation Society of America, Ankeny, Iowa.

Liang, T. T. and Lichtenstein, E. P. (1972) Effect of light, temperature, and pH on the degradation of azinphosmethyl. J. Econ. Entomol. 65, 315-321.

Liang, T. T. and Lichtenstein, E. P. (1976) Effects of soils and leaf surfaces on the photodecomposition of [^{14}C] azinphosmethyl. J. Agric. Food Chem. 24, 1205-1210.

Manetsch, T. J. 1976. Time-varying distributed delays and their use in aggregate models of large systems. IEEE Trans. Systems, Man, and Cybern., SMC-6, pp. 547-553.

Matsumurs, Fumio. 1975. Toxicology of Insecticides. Plenum Press, New York, 503 p.

McMechan, A. D., Morgan, C. V. G. and Wardle, G. A. (1972) Erosion of azinphosmethyl from apple leaves by rain and overtree irrigation. J. Entomol. Soc. Brit. Columbia, 69, 5-8.

McQueen, D. J. 1976a. *Porcellio spinicornis* SAY (Isopoda) demography. II. A comparison of field and laboratory data. Can. J. Zool. 54: 825-842.

McQueen, D. J. 1976b. *Porcellio spinicornis* SAY (Isopoda) demography. III. A comparison between field data and the results of a simulation model. Can. J. Zool. 54:2174-2184.

McQueen, D. J. 1976c. The influence of climatic factors on the demography of the terrestrail isopod *Tracheoniscus rathkei* BRANDT. Can. J. Zool. 54:2185-2199.

McQueen, D. J. and J. S. Carnio. 1974. A laboratory study of the effects of some climatic factors on the demography of the terrestrial isopod *Porcellio spinicornis* SAY. Can. J. Zool. 52:599-611.

Menzie, C. M. 1972. Fate of pesticides in the environment. Ann. Rev. Ent. pp. 199-221.

Merriam, H. G. 1971. Sensitivity of terrestrial isopod populations (*Armadillidium*) to food quality differences. CAn. J. Zool. 49: (5), pp. 667-674.

Morris, M. G. 1968. Differences between the invertebrate faunas of grazed and ungrazed chalk grasslands. II. The fauna of sample turfs. J. Appl. Ecol. 5:601-611.

Murchie, W. R. 1960. Biology of the oligochaete Bimastos zeteki Smith and Gittins (Lumbricidae) in Northern Michigan. Amer. Midl. Natur. 64: 194-215.

National Academy of Sciences. 1969. Insect Pest Management and Control. Publ. 1695. Washington, D. C. 508 pp.

Nigg, H. N., Allen, J. C., King, R. W., Thompson, N. P., Edwards, G. J. and Brooks, R. F. (1977) Dislodgeable residues of ethion in Florida citrus and relationships to weather variables. Arch. Environ. Contam. Toxicol. 6, 257-267.

Nilles, G. P. and Zabik, M. J. (1975) Photochemistry of bioactive compounds. Multiphase photodegradation and mass spectral analysis of basagran. J. Agric. Food Chem. 23, 410-414.

NSF/RA. (1976) Ecosystem processes and organic contaminants, research needs and an interdisciplinary perspective. NSF/RA 760008.

Odom, E. P. 1971. Fundamentals of Ecology. 3rd Edition. W. B. Saunders Co. Philadelphia. 547 pp.

Ouellette, R. P. and J. A. King. 1977. Chemical week Pesticides Register. McGraw-Hill Book Co. New York. 346 pp.

Paris, O. H. and F. A. Pitelka. 1962. Population characteristics of the terrestrial isopod *Armadillidium vulgare* in California grassland. Ecol. 43(2). pp. 229-248.

Parmele, L. H., Lemon, E. R. and Taylor, A. W. (1972) Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions. Water Air Soil Poll. 1, 433-451.

Phillips, F. T. T. (1971) Persistence of organochlorine insecticides on different substrates under different environmental conditions. I. The rates of loss of dieldrin and aldrin by volatilization from glass surfaces. Pestic. Sci. 2, 255-266.

Phillips, F. T. (1974) Some aspects of volatilization of organochlorine insecticides. Chem. Ind. 5, 197-201.

Pielou, F. C. (1969) An Introduction to Mathematical Ecology. Wiley Interscience, New York, p. 19-22.

Pimentel, D. and Goodman, N. (1974) Environmental impact of pesticides. In Survival in Toxic Environments. (Eds. Khan, M. A. Q. and Bederka, J. B., Jr.) 25-52.

Plimmer, J. R., Kearney, P. C., Kaufman, D. D. and Guardia, F. S. (1967) Amitrole decomposition by free radical generating systems and by soils. J. Agric. Food Chem. 15, 996-999.

Popendorf, W. J. and Leffingwell, J. T. (1978) Natural variations in the decay and oxidation of parathion foliar residues. J. Agric. Food Chem. 26, 437-441.

Pregitzer, K. E. and J. R. Stacey. 1973. Soil Survey, Alpine Township, Kent County, Michigan. Publ. Soil Conservation Service, U.S. Dept. of Agriculture.

Ritter, W. F., Johnson, H. P., Lovely, W. G. and Molnau, M. (1974) Atrazine, propachlor, and diazinon residures on small agricultural watersheds, runoff losses, persistence and movement. Environ. Sci. Technol. 8, 38-42.

Rohrbaugh, W. J., Meyers, E. K. and Jacobson, R. A. 1976. Crystal and molecular structure of organophosphorus insecticides.

Saltzman, S., L. Kliger and Yaron, B. (1972) Adsorption-desorption of parathion as affected by soil organic matter. J. Agric. Food Chem. 20, 1224-1226.

Satchell, J. E. 1967. Lumbricidae. In: Burges and Raw, eds., Soil Biology. Acad. Press, London, pp. 259-322.

Schrader, G. (1963) Die entwichlung neuer insecktizider phosphazaure-ester. Weinhein/Bergstr.: Verlag Chemie GmbH.

Schulz, K. R., Lichtenstein, E. P., Liang, T. T. and Fuhrmann, T. W. (1970) Persistence and degradation of azinphosmethyl in soils, as affected by formulation and mode of application. J. Econ. Entomol. 63, 432-438.

Scopes, N. E. A. and E. P. Lichtenstein. 1967. The use of Folsomia fimetaria and Drosophila melanogaster as test insects for the detection of insecticide residues. J. Econ. Entom. 60 (6):1539-1541.

Smith, R. F. 1976. Insecticides and integrated pest management. In the Future for Insecticides, Needs and Prospects. Wiley Interscience, New York, pp. 489-506.

Smith, A. E. and Walker, A. (1977) A quantitative study of asulam persistence in soil. Pestic. Sci. 8, 449-456.

Smith, J. H., Mabey, W. R., Bohonos, N., Holt, B. R., Lee, S. S., Chou, T. W., Bomberger, D. C. and Mill, T. (1977) Environmental Pathways of Selected Chemicals in Freshwater Systems. EPA Report 600/7-77-113.

Snider, R. M. (1979) The effects of azinphosmethyl (Guthion®) on a population of Trachelipus rathkei (Isopoda) in a Michigan orchard. Pedobiol. 19, 99-105.

Snider, R. M. and Shaddy, J. W. (1980) The ecobiology of Trachelipus rathkei (Isopoda). Pedobiol. 20, 394-410.

Wouthwick, C. H. (1976) Ecology and the Quality of Our Environment. 2nd Ed., D. Van Nostrand, London. 426 p.

Spear, R. C., Y. Lee, J. T. Leffingwell and D. Jenkins. 1978. Conversion of parathion to paraoxon in foliary residues: effects of dust level and ozone concentration. J. Ag. Food Chem. 26:434-436.

Spencer, W. F. and M. M. Claith. 1969. Vapor density of dieldrin. Environ. Sci. Tech. 3:670-674.

Spencer, W. F. ans M. M. Claith. 1975. Vaporization of chemicals. In Environmental Dynamics of Pesticides. (R. Haque and V. H. Freed, Eds.) p. 61-78. Plenum Press. New York.

Spencer, W. F. and Claith, M. M. (1977) The solid-air interface: transfer of organic pollutants between the solid-air interface. In Fate of Pollutants in the Air and Water Environments, Part I. (Ed. Suffet, I. H), P. 107-126. John Wiley and Sons, Inc., New York.

Spencer, W. F., Farmer, W. J. and Claith, M. M. (1973) Pesticide Volatilization. Residue Reviews 49, 1-47.

Stamper, J. H., H. N. Nigg, and J. C. Allen. 1979. Organophosphate insecticide disappearance from leaf surfaces: an alternative to first-order kinetics. Environ. Sci. Tech. 13:1402-1405.

Steffens, W. and Wieneke, J. (1975) Influence of humidity and rain on uptake and metabolism of ^{14}C-azinphosmethyl in bean plants. Arch. Environ. Contam. Toxicol. 3, 364-370.

Steffens, W. and J. Wieneke. (1976) Studies on the uptake, metabolism and degradation of ^{14}C-labelled ^{R}Gusathion in kidney beans. Pfanzenschultz-Nachrichten 29, 1-17.

Steiner, P. W. (1969) The distribution of spray material between target and non-target areas of a mature apple orchard by airblast equipment. M.S. Thesis, Cornell Univ.

Sutton, S. L. 1968. The population dynamics of *Trichoniscus pusillus* and *Philoscia muscorum* (Crustacea: Oniscoidea) in limestone grassland. J. Anim. Ecol. 37:425-444.

Taylor, A. W. (1978) Post-application volatilization of pesticides under field conditions. J. Air Poll. Control Assoc. 28, 922-927.

Taylor, A. W., Glotfelty, D. E., Glass, B. L., Freeman, H. P. and Edwards, W. M. (1976) Volatilization of dieldrin and heptachlor from a maize field. J. Agric. Food Chem. 24, 625-631.

Taylor, A. W., Glotfelty, D. E., Turner, B. C., Silver, R. E., Freeman, H. P. and Weiss, A. (1977) Volatilization of dieldrin and heptachlor residues from field vegetation. J. Agric. Food Chem. 25, 542-548.

Teskey, B. J. E. and J. S. Shoemaker, 1978. Tree Fruit Production. AVI Publishing Co., Inc. Westport, CT. pp. 19-25.

Thompson, A. R. and F. I. Gore. 1972. Toxicity of 29 insecticides to *Folsomia candida*. Laboratory studies. J. Econ. Entom. 65:1255-1260.

Thompson, A. R. 1973. Persistence of biological activity of seven insecticides in soil assayed with *Folsomia candida*. J. Econ. Entom. 66 (4):855-857.

Thompson, N.P. and Brooks, R. F. (1976) Disappearance of dislodgeable residues of five organophosphate pesticides on cirtrus leaves and fruit during dry and wet weather in Florida. Arch. Environ. Contam. Toxicol. 5, 55-61.

Tomlin, A. D. 1975. Toxicity of soil applications of insecticides to three species of Springtails (Collembola) under laboratory conditions. Can. Ent. 107:769-774.

Turner, B. C. and Glotfelty, D. E. (1977) Field air sampling of pesticide vapors with polyurethane foam. Anal. Chem. 49, 7-10.

Van Dyk, L. P. (1974) The persistence of some pesticides on South African citrus. Environ. Qual. Safety, suppl. III, p. 330-335.

Van Dyk, L. P. (1976) Parathion persistence on South African citrus. Arch. Environ. Contam. Toxicol. 4, 2389-311.

Van Rhee, J. A. 1977. Effects of soil pollution on earthworms. Pedobiol. 17:201-209.

Van Rhee, 1961.

Verhoeff, K. W. 1920. Zur Kenntnis der Larven, des Brutasackes und der Bruten der Oniscoidea-Isopoden. Aufsätze 28. Zool. Anz. 51:169-189.

Walker, A. (1974) A simulation model for the prediction of herbicide persistence. J. Environ. Quality 3, 396-401.

Walker, A. (1976a) Simulation of herbicide persistence in soil. I. Simazine and Prometryne. Pestic. Sci. 7, 41-49.

Walker, A. (1976b) Simulation of herbicide persitence in soil. II. Simazine and Linuron Long-Term Experiments. Pestic. Sci. 7, 50-58.

Walker, A. (1976c) Simulation of herbicide persistence in soil. III. Propyzamide in Different Soil Types. Pestic. Sci. 7, 59-64.

Walker, A. and A. Barnes. 1981. Simulation of herbicide persistence in soil: a revised computer model. Pest. Sci. 12:123-132.

Walker, A. and A. E. Smith. 1979. Persistence of 2,4,5-T in a heavy clay soil. Pest. Sci. 10:151-157.

Waters, R. A. S. 1955. Numbers and weights of earthworms under a highly productive pasture. N. Z. J. Sci. Techn., Sect. A: Agric. Res., 36:516-525.

Welch, B. L. 1938. The significance of the difference between two means when the population variances are unequal. Biometrika 29:350-362.

White, A. W., Jr., Harper, L. A., Leonard, R. A. and turnbull, J. W. (1977) Trifuluralin volatilization losses from a soybean field. J. Environ. Qual. 6, 105-110.

White, J. J. 1968. Bio-energetics of the woodlouse *Tracheonisucus rathkei* BRANDT in relation to litter decomposition in a deciduous forest. Ecology 49:695-704.

Whittaker, R. H. (1975) Communities and Ecosystems. MacMillan Publishing Co., New York.

Wieneke, J. and Steffens, W. (1974) Degradation of ^{14}C-azinphos on glass plates as compared to the metabolism on bean leaves. Environ. Qual. Safety, Suppl. III., 544-548.

Williams, K. (1961) Note on the effect of rain, and sprinkler irrigation, on the persistence of spray residues of Guthion and Sevin on apple leaves. Can. J. Plant Sci. 41, 449-451.

Winterline, W., Bailey, J. B., Langbehn, L. and Mourer, C. (1975) Degradation of parathion applied to peach leaves. Pest. Mont. J. 8, 263-269.

Woodrow, J. E., Seiber, J. N., Crosby, D. G., Moilanen, K. W., Soderquist, C. J. and Mourer, C. (1977) Airborne and surface residues of parathion and its conversion products in a treated plum orchard environment. Arch. Environ. Contam. Toxicol. 6, 175-191.

Yaron, B., Hever, B. and Birk, Y. (1974) Kinetics of azinphosmethyl losses in the soil environment. J. Agric. Food Chem. 22, 439-441.

Zabik, M. J. and L. O. Ruzo. (1981) Factors Affecting Pesticide Photodecomposition Studies. In Test Protocols for Environmental Fate and Movement of Toxicants, p. 20-27. Proc. Symp. 94th Ann. Meeting Ass. of Offic. Anal. Chemists, Washington, D.C.

Zabik, M. J., Leavitt, R. A. and Su, G. C. (1976) Photochemistry of bioactive compounds: a review of pesticide photochemistry. Ann. Rev. Entomol. 21, 61-79.

Zepp, R. G., Wolfe, N. L., Gordon, J. A., and Baughman, G. L. (1975) Dynamics of 2,4-D esters in surface waters hydrolysis, and vaporization. Environ. Sci. Tech. 9, 1144-1150.

Zepp, R. G. and Cline, David M. (1977) Rates of direct photolysis in aquatic environment. Environ. Sci. Tech. 11, 359-366.

APPENDIX A

Running the Process and Orcdata Data Analysis Routines

This appendix is intended only to document the process in which data were prepared for analysis and use in parameterizing the models described in this report. These routines are written to run only on MSU's CYBER 750 Computer, and are not intended for use by others. The appendix consists of brief descriptions of programs utilized and the control card structures needed to run them. It does not address the data used in parameterizing the organism models.

Process

The binary for processing the data (adding of data, duplicate check, error correction and statistics) is on file PROCESSBIN.

IRUNMOD gives the user choice of routines to be used.

IRUNMOD

1 = Addition of data to existing data files (ADD)
2 = Search for duplicates and delete oldest copy of duplicates found (DUP)
3 = Processing of samples (PROCESS)
4 = Processing of targets (rain and non-rain) (PROTARG)

It is suggested that if IRUNMOD (1) is chosen, IRUNMOD (2) should also be chosen.

ADD and DUP use these files:

Tape 2 = DATASAMPLES
Tape 3 = DATATARGETS
Tape 4 = NONRAINTARGETS
and put out these files
Tape 20 = DATASAMPLES
Tape 21 = DATATARGETS
Tape 22 = NONRAINTARGETS
PROCESS uses these files:
Tape 20 = DATASAMPLES
Tape 48 = SPRAYDATES
Tape 49 = RAINDATES
and puts out this file:
Tape 23 = PROCESSEDSAMPLES
PROTARG uses these files:
Tape 21 = DATATARGETS
Tape 22 = NONRAINTARGETS
and puts out these files:
Tape 24 = PROCESSEDTARGETS
Tape 25 = PROCESSEDNONRAIN

To run this program attach the files needed for the routines that are desired

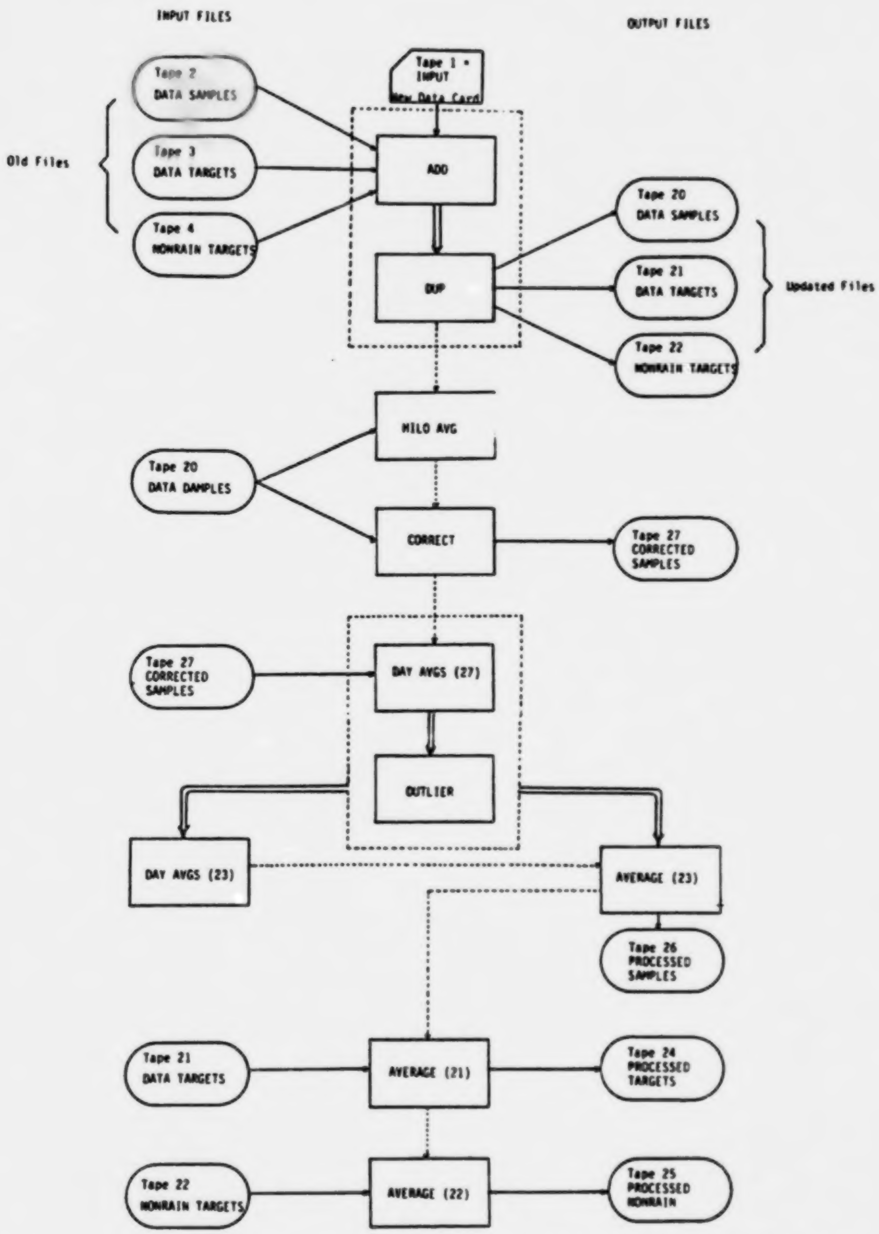

INPUT FILES
OUTPUT FILES
Tape 1 = INPUT
New Data Card
Tape 2
DATA SAMPLES
Old Files
Tape 3
DATA TARGETS
Tape 4
NONRAIN TARGETS
ADD
DUP
Tape 20
DATA SAMPLES
Tape 21
DATA TARGETS
Tape 22
NONRAIN TARGETS
Updated Files
HILO AVG
Tape 20
DATA DAMPLES
CORRECT
Tape 27
CORRECTED
SAMPLES
Tape 27
CORRECTED
SAMPLES
DAY AVGS (27)
OUTLIER
DAY AVGS (23)
AVERAGE (23)
Tape 26
PROCESSED
SAMPLES
Tape 21
DATA TARGETS
AVERAGE (21)
Tape 24
PROCESSED
TARGETS
Tape 22
NONRAIN TARGETS
AVERAGE (22)
Tape 25
PROCESSED
NONRAIN

Figure A-1. Flowchart of the processing of raw data to create processed files.

and then attach the binary on file PROCESSBIN. If the ADD and DUP parts of the program are being used, this card must be included before execution of the program:

```
LDSET,LIB = FORTRAN/CRM.
```

This card is necessary any time sort/merge is used.

After execution of the program, purge off the previous files and catalog the new files created.

After the control cards, the first card of the data is IRUNMOD in a 10I1 format with a "1" for each part of the program desired and a "0" input otherwise.

After the IRUNMOD card, place the data to be added (if the ADD and DUP routines are selected).

Example:

If execution of the entire program is desired, use the following sequence of cards:

```
ATTACH, TAPE 2, DATASAMPLES, PW=...
ATTACH, TAPE 3, DATATARGETS, PW=
ATTACH, TAPE 4, NONRAINTARGETS, PW=
ATTACH, TAPE 48, SPRAYDATES, PW=
ATTACH, TAPE 49, RAINDATES, PW=
ATTACH, BIN, PROCESSBIN, PW=
LDSET, LIB=FORTRAN/CRM.
BIN.
PURGE, TAPE 2.
CATALOG, TAPE 20, DATASAMPLES, PW=...., RP=999.
PURGE, TAPE 3.
CATOLOG, TAPE 21, DATATARGETS, PW=..., RP=999.
PURGE, TAPE 4.
CATALOG, TAPE 21, DATARGETS, PW=..., RP=999.
PURGE, TAPE 4.
CATALOG, TAPE 22, NONRAINTARGETS, PW=..., RP=999.
ATTACH, A, PROCESSEDSAMPLES, PW=
PURGE, A.
CATALOG, TAPE 26, PROCESSDSAMPLES, PW=..., RP=999.
ATTACH, B, PROCESSEDTARGETS, PW=
PURGE, B.
CATALOG, TAPE 24, PROCESSED TARGETS, PW=...,RP=999.
ATTACH, C, PROCESSEDNONRAIN, PW=
PURGE, C.
CATALOG, TAPE 25, PROCESSED NONRAIN, PW=...,RP=999.
```

```
7
 8
  9
1111111

______
______
______   Data cards to be added
______
______
______
6
 7
  8
   9
```

Whenever the raw data files are changed be sure to check the files to assure that they are correct. If something went wrong with the program so that the data are lost, there are backup files for the raw sample and raw target files called DATASAMPLESBACKUP and DATATARGETSBACKUP respectively. After making sure the data were added correctly and is on permanent files, purge the backup files, make copies of the new data files and catalog these copies under the name DATASAMPLESBACKUP and DATATARGETSBACKUP. These files contain all the data upon which the orchard model is based so be careful not to lose them.

ALSO, back up the file NONRAINTARGETSBACKUP in a similar manner.

Subroutine ADD

Sorts the new data into samples, targets, and nonrain targets and then merges the new data with the appropriate file (DATASAMPLES, DATATARGETS or NONRAINTARGETS).

Targets are distinguished from samples by checking column seven of the data card. All target data have a 6 in column 7 while sample data have a number less than 6 in column 7.

Nonrainfall targets have a 1 in column 25 while spray targets have a blank in column 25.

A description of the Fortran - Sort/Merge Interface can be found in section III-16 of the CDC Cyber Fortran Reference Manual.

Inputs to ADD

TAPE 2 = INPUT: New Data Cards to be added
TAPE 2 : DATASAMPLES   files to be updated
TAPE 3 : DATATARGETS
TAPE 4 : NONRAINTARGETS

Outputs

TAPE 11 : Raw Samples with new samples added
TAPE 12 : Raw Targets with new targets added
TAPE 13 : Raw Nonrain targets with new non-rain targets added

Subroutine DUP

DUP checks the data files for duplicates. Any two cards which have the same first 13 characters are considered duplicates.

When duplicates are located the copy with the greatest number of blanks is deleted. (In other words, the card with the most data is retained.)

DUP prints out which cards are deleted from the file and which cards are kept. This listing should be checked to make sure the proper cards were deleted.

Inputs to DUP

TAPE 11 : Raw Samples
TAPE 12 : Raw Targets   Output files from ADD containing duplicates
TAPE 13 : Non-rain Targets

Outputs

TAPE 20 : DATASAMPLES
TAPE 21 : DATATARGETS These files should be catalogued
TAPE 22 : NONRAINRAGETS

Subroutine HILOAVG

HILOAVG computes the ratio of the average amount of dislodgeable residue per leaf surface area in the entire tree to amount of residue found in the bottom portion of the trees. It does this by analyzing leaf samples from year 3 (1978) as this was the first year that samples were taken from the upper portion of the tree.

Leaf sample data cards have a 1 in column 10 if the sample was taken from the upper portion of the tree. Samples taken from the lower portion of the tree have a blank or a 2 in column 10 of the card.

To find the ratio of average tree to bottom tree amounts HILOAVG finds the average for both upper and lower tree values for each plot on a single day. The average tree value is then taken to be the average of the value found for the upper tree and the value for the lower tree.

$$\text{Avg. Tree Residue} = \frac{\Sigma TOP/N_1 + \Sigma BOTTOM/N_2}{2}$$

where N_1 is the number of upper tree samples and N_2 is the number of bottom tree samples. The Ratio is then calculated by dividing this average tree value by the average value found for the lower tree.

HILOAVG then computes a rate at which the ratio decreases per day during rainfall and non-rainfall intervals.

The ratio and the rate of change of the ratio are eventually going to be used to calculate the average tree residue amounts from bottom tree samples for years 1 and 2 (1976 and 1977).

Inputs to HILOAVG

TAPE 20 : PROCESSEDSAMPLES

Output: Currently output to printer only.

Subroutine CORRECT

CORRECT checks for soil samples and then makes corrections for:

(1) weight extracted .LT. total weight
(2) % efficiency of extraction
(3) % efficiency of column cleanup

TFRWT = WTEXT + WTCOR
PENRES = TFRWT * PENRES/WT EXT
RESIDUE = PENRES * 1.1765 * 7.008
or
1.3072

$$7.008 = \frac{210.25\ cm^2 \quad \text{(area of sample)}}{3 \times (10\ cm^2 \quad (10\ cm^2 = \text{area of core sample}))}$$

1.1765 = 1/.85 (.85 = Extraction efficiency)

1.3072 = 1/(.85*.9) (.9 = column cleanup efficiency)

CORRECT also makes similar corrections for grass, litter, and moss.

Samples which, in comparison with others of the same type (e.g., region and day) are determined to be statistical outliers, and discarded before the PROCESSED files are created. Only grass and soil samples are subjected to outlier procedures, because tree and litter/moss samples are already assembled from multiple samples (e.g., upper/lower tree leaves, sums of litter and moss) so the outlier procedure was not easily employed.

Example of Outlier processing

$$\mathrm{MSE} = \mathrm{SSE}/(n-t)$$

$$\mathrm{SSE} = (SS_y - SS_T) = \sum_{i=1}^{t} \left(\sum_{j=1}^{n} Y_{ij}^2 \right) - \sum_{i=1}^{t} (Y_{i.}^2/n_i)$$

$Y_1 = .200$

$Y_2 = .387$ $\quad t = 1 \quad n_i = n = 3$

$Y_3 = .209$

$\Sigma Y_i = .796$

$\bar{Y}_i = .265$

$$\Sigma\Sigma Y_{ij}^2 = (.200)^2 + (.387)^2 + (.209)^2 = .233$$

$$\Sigma Y_{i.}^2/n_i = (.796)^2/3 = .211$$

$$\mathrm{SSE} = .233 - .211 = .022$$

$$\mathrm{MSE} = .022/(3-1) = .011$$

$$e_L = (Y_{ij} - \bar{Y}_{i.}) = .387 - .265 = .122$$

OUTLIER TEST → $e_L/\sqrt{MS_E} = .122/\sqrt{.011}$

$= 1.16$

$Y_{ij} = .387$ is OUTLIER with $\alpha = 2.01$, because

1.160 > 1.155 (TEST STAT. FROM TABLE A -1)

Table A-1. Critical Values for
Testing an Outlying Observation

n	α=0.01	0.05	0.10	n	α=0.01	0.05	0.10
...	...	...	...	32	3.135	2.773	2.591
...	...	...	...	34	3.164	2.799	2.616
3	1.155	1.153	1.148	36	3.191	2.823	2.639
4	1.492	1.463	1.425	38	3.216	2.846	2.661
5	1.749	1.672	1.602	40	3.240	2.866	2.682
6	1.944	1.822	1.729	42	3.261	2.887	2.700
7	2.097	1.938	1.828	44	3.282	2.905	2.719
8	2.221	2.032	1.909	46	3.302	2.923	2.736
9	2.323	2.110	1.977	48	3.319	2.940	2.753
10	2.410	2.176	2.036	50	3.336	2.956	2.768
11	2.485	2.234	2.088	55	3.376	2.992	2.804
12	2.550	2.285	2.134	60	3.411	3.025	2.837
13	2.607	2.331	2.175	65	3.442	3.055	2.866
14	2.659	2.371	2.213	70	3.471	3.082	2.893
15	2.705	2.409	2.247	75	3.496	3.107	2.917
16	2.747	2.443	2.279	80	3.521	3.130	2.940
17	2.785	2.475	2.309	85	3.543	3.151	2.961
18	2.821	2.504	2.335	90	3.563	3.171	2.981
19	2.854	2.532	2.361	95	3.582	3.189	3.000
20	2.884	2.557	2.385	100	3.600	3.207	3.017
21	2.912	2.580	2.408	105	3.617	3.224	3.033
22	2.939	2.603	2.429	110	3.632	3.239	3.049
23	2.963	2.624	2.448	115	3.647	3.254	3.064
24	2.987	2.644	2.467	120	3.662	3.267	3.078
25	3.009	2.663	2.486	125	3.675	3.281	3.092
26	3.029	2.681	2.502	130	3.688	3.294	3.104
27	3.049	2.698	2.519	135	3.700	3.306	3.116
28	3.068	2.714	2.534	140	3.712	3.318	3.129
29	3.085	2.730	2.549	145	3.723	3.328	3.140
30	3.103	2.745	2.563				

Values were extracted from Grubbs and Beck, Technometrics 14:847-854 (1972).

Record Formats (Card Images) for Raw Corrected, and Processed Files.

Table A-2. Raw Files - data samples, data targets, non-rain targets

Column	Description	Format I or F
1	year	I
2	spray periods	I
3	sample period within spray	I
4-6	julian date	I
7	layer	I
8-9	plot #	I
10	(for yr. 3 leaves) upper or lower leaf sample	I
11-12	lab. code #	I
13	region	I
14-17	yr., date of extraction	I
18-21	yr., date of analysis of dislodgeable	I
22-27	extracted fresh wt. in gms.	F
28-33	extracted dry wt. in gms.	F
34-39	penetrated residue (g/cm^2) soils acetones	F
40-45	dislodgeable residue (/cm^2) lvs., moss, grass, soil, litter, targets	F
46-51	area of sample in cm^2 (if area ≠ 210.25 cm^2)	F
52-57	SOILS / moisture sample wt. before dry	F
58-63	SOILS / moisture sample wt. after dry	F
64	set # for targets	I
65-70	total sample fresh wt. in gms.	F
71	= 1 if residue analyzed	I
72	column clean up flag	I
73	fleaker flag	I
74	sample #	I
75-78	yr., data acetone g.c.	I
79	if soil	I
80	if sample cup empty	I

Table A-4. Processed Files - targets, samples, non-rain targets.

Column	Description	Format I or F
1	year	I
2	spray period	I
3	sample period	I
4-6	julian date	I
7	layer	I
8-9	plot #	I
13	region	I
21-22	# samples	I
23-31	avg. penetrated residue	F
32-40	std. dev. of penetrated samples	F
41-49	std. error of penetrated sampled	F
50-58	sum of squares of penetrated samples	F
61-62	# dislodgeable samples	I
63-71	avg. dislodgeable residue	F
72-80	std. dev. of dislodgeable samples	F
81-89	std. error of dislodgeable samples	F
90-98	sum of squares of dislodgeable samples	F

ORCDATA, The Parameterization Routines

Figure A-2 shows the data flow through the parameterization routines. The control card structure to run the ORCDATA program is shown below:

```
ATTACH, BIN, ORCDATABIN, PW = APPLE.
BIN.
789
Data input
6789
```

Input card sequence
1) Beginning and ending year of span to be studied (212)
2) IRUNMOD (1 if routine is desired, 0 otherwise) (2011)

Example: If spray distribution from analysis of samples and targets for years 1 and 2 is desired, use these cards.

```
ATTACH, BIN, ORCDATABIN, PW = APPLE.
BIN.
789
1 2
0000000000000100000
6789
```

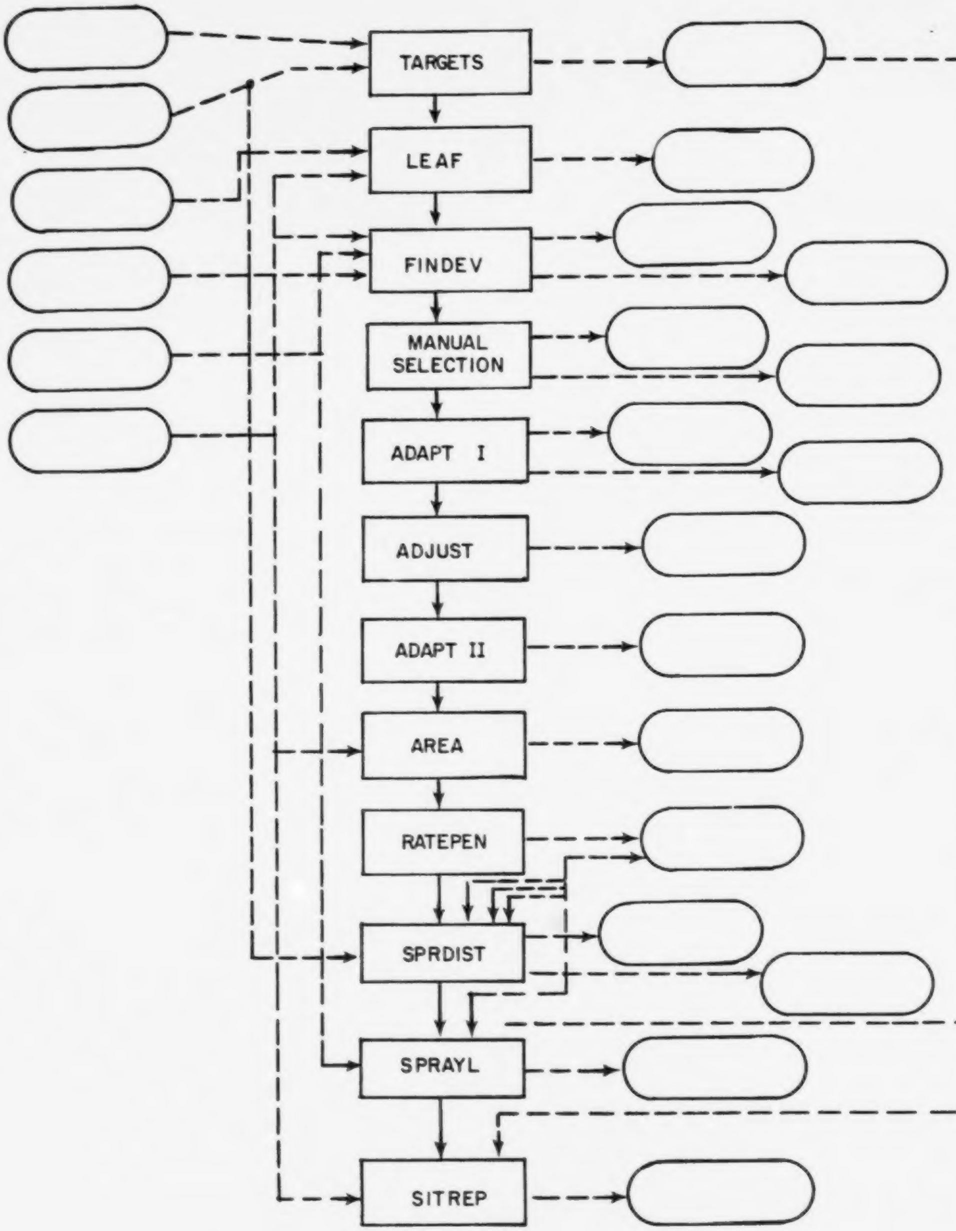

TARGETS
LEAF
FINDEV
MANUAL SELECTION
ADAPT I
ADJUST
ADAPT II
AREA
RATEPEN
SPRDIST
SPRAYL
SITREP

Figure A-2. Data flow in parameterization routines (ORCDATA).

Unit numbers for ORCDATA - these files are attached, purged, and recatalogued inside the program itself.

TAPE	PERMANENT FILE
1	PROCESSED SAMPLES
2	PROCESSED TARGETS
3	PLOTAREAS
4	SPRAYRATES
5	TREEINTERCEPTINDEX
7	SAMPLEDATES
8	SPRAYDATES
9	RAINDATES
14	PESTDIST
16	PENETRATIONRATES
L&	NRMOVE -
18	SITUATIONREPORT
19	PAIREDDATASAMPLES -

IRUNMOD	SUBMODEL
1	
2	
3	
4	Penetration
5	
6	
7	Leaf Areas
8	
9	
10	
11	
12	
14	Spraydistribution Analysis & targets
15	Spray 1 Analysis of samples
16	
17	Alternate Spray 1 calculations
18	Situation Report
19	
20	Non-rain & rain intervals

Subroutine Leaf

Leaf calculates the tree intercept index for each plot from measured leaf area per tree, number of trees per plot, and areas of canopy regions in each plot.

Measured leaf area per tree is a constant equal to 4×10^5 cm.^{2}, calculated by removing all the leaves from a representative tree, counting them, and multiplying by the average area per leaf.

The leaf area index "LAI" is calculated by

$$LAI_i = \frac{NTREES_i \times LAPTREE}{CANOPY\ AREA_i}$$

where: $NTREES_i$ = # of trees in plot i

LAPTREE = leaf area per tree = 4×10^5 cm.^{2}

$CANOPY\ AREA_i$ = ground area of canopy region for plot i

The tree intercept index "TII" is equal to the LAI multiplied by 1.15. This is based on the assumption that the trunk region is 15% of the leaf area index.

Input files used
tape 3: plot areas

Output files
tape 5: tree intercept index, format = 6F10.3

Subroutine Targets

Targets use target samples to calculate the average amount of pesticide (in µg/cm^2) for a given year, region (alleys 1 throguh 3, canopy, trunk), plot (3 through 6) based on the distribution of targets for the first spray period of each spray (i.e., only spray dates). It also calculates the standard deviation, standard error, sample size for each average, and HPESTD", the proportion of pesticide allocated to each region of a plot per dose applied to that plot; along with "HCANOPY", the proportion of spray not accounted for, or allocated to canopy leaves.

Input files used

tape 2: processed targets

tape 3: plot areas

tape 4: sprayrates

Output files - none

HPESTD, the proportion of pesticide allocated to a given region of a plot per dose of pesticide applied to that plot for a specific year is calculated by

$$HPESTD_{ij} = \frac{\sum_{k=1}^{NSPRAYS} \frac{AVGT_{ijk} \times AREA_{ij}}{AMTSPRAY_{ik}}}{NSPRAYS}$$

where: NSPRAYS = # of sprays for that year

$AVGT_{ijk}$ = average pesticide in $\mu g/cm^2$ for plot i, region j, on spray number k

$AREA_{ij}$ = proportion of aea of region j of plot i

$AMTSPRAY_{ik}$ = amount of pesticide in $\mu g/cm^2$ sprayed to plot i on spray number k.

HCANOPY, the proportion of spray not accounted for is calculated by

$$HCANOPY_i = 1.0 - DRIFT - \sum_{j=1}^{NREGIONS} HPESTD_{ij}$$

where: DRIFT = average proportion of drift for the specific year, from subroutine ALLOC, assumed to be the average proportion for each plot

NREGIONS = # of horizontal regions (alleys 1-3, canopy, trunk) = 5.

SUBROUTINE SPRAY 1

SPRAY 1 analyzes the first spray of each year from data samples. It calculates the average amount of pesticide in $\mu g/cm^2$ for each year, region (including trunk, canopy, and alley, where alley regions 1 through 3 merged into one region) and plot (3 through 6). It also gives the standard deviation, standard error, and sample size for each average, and "VPESTD," the proportion of pesticide applied to each region and layer of a plot per dose of pesticide applied to that plot.

If IRUNMOD (17) is turned off (i.e., IRUNMOD (17) = 0), some additional spray calculations are made which use initial penetration rates.

(1) the vertical proportions of pesticide in each plot, layer, and region per dose of pesticide applied, "VPESTD," is averaged over plots to give "PROPD," the proportion of pesticide (dislodgeable) for each layer (1 through 5) and each region (alley and canopy; here trunk is assumed to be included in canopy region) per dose of pesticide applied.

$$PROPD_{jk} = \frac{\sum_{i=3}^{NPLOTS} VPESTD_{ijk}}{NPLOTS}$$

PROPP, the proportion of pesticide (penetrated) for each layer (1 through 5) and region (alley, canopy) per dose of pesticide applied, is estimated using initial penetration rates for each layer

$$PROPP_{jk} = \frac{INITPEN_k * PROPD_{jk}}{(1.0 - INITPEN_k)}$$

where $INITPEN_k$ is ratio of penetrated residue to total residue (penetrated+ dislodgeable) for layer k on the first spray of a season.

Next Airloss is estimated as the proportion not accounted for

$$\text{Airloss} = 1.0 - \sum_{i=1}^{\text{NLAYERS}} \left(\sum_{j=1}^{\text{NREGIONS}} (\text{PROPD}_{ij} + \text{PROPP}_{ij}) \right)$$

(2) Airloss is calculated on a plot by plot basis using targets to calculate the proportion reaching the ground and leaf samples to calculate the proportion going to the tree.

$$\text{AIRLOSS}_i = 1.0 - \sum_{j=1}^{\text{NALLOPY}} \text{HPESTD}_{ij} - \text{VLEAF}_i$$

where

AIRLOSS_i is the airborne loss from plot_i

HPESTD is described in subroutine TARGETS description

$$\text{VLEAF}_i = \underbrace{\left[\frac{(\text{VPESTD}_{i41} + \text{VPESTD}_{i51})}{1.15} \right]}_{\text{Q1}} \underbrace{\left[1 + \frac{\text{INITPEN}(1)}{(1 - \text{INITPEN}(1))} \right]}_{\text{Q2}}$$

Q1, quantity 1 is the vertical proportion of pesticide allocated to the canopy leaves plus trunk leaves regions per dose applied to that plot as previously calculated by SPRAY1. Since the trunk region is summed in with the canopy, the sum must be divided by 1.15 which moves the 15% assumed trunk area when the tree intercept index was applied, Q2, accounts for penetrated residue of leaf values

(3) Finally some calculations are made which have to do with how much pesticide is in the ground layers. The proportion of proportion of dislodgable residue in the ground layers out of the total dislodgable residue (all layers) is calculated for each ground layer out of the total dislodgable residue in all ground layers (layers 1 through 4) is calculated for the canopy and alley regions.

If IRUNMOD (17) is turned on (i.e. IRUNMOD (17) = 1), averages and vertical proportions, "VPESTD," will be calculated based on the sum of measured dislodgable and penetrated averages.

Input Files Used

tape 1:	processed samples
tape 2:	processed targets
tape 3:	plot areas
tape 4:	spray rates
tape 16:	penetration rates

Output Files - none

Subroutine Sprdist

Sprdist is used to estimate drift and spray distribution. It uses only first spray dates of a season and other spray dates that have a non-rain interval between the preceding sample date and that spray date. If the interval between the sample date and the spray date is a rainfall period, it is flagged in output saying it cannot be used.

The following steps describe the procedure for estimating the drift and spray distribution.

(1) The non-rain movement matrix is applied to sample values of the sample date preceding a spray date to give the amount of pesticide present immediately before the spray occurs. If a spray date is the first of the season these values are all zero.

(2) The amounts of pesticide before the spray are subtracted from the sample values of the spray date in each region and layer. This gives the contribution of dislodgable residue (in $\mu g/cm^2$) on that date giving the proportion of pesticide in each compartment to the total amount of pesticide applied.

(4) Proportion drift for this spray is estimated to be 1 minus the sum of the proportions of pesticide applied to each compartment.

Input files used

tape 1 : processed samples
tape 4 : spray rates
tape 3 : plot areas
tape 7 : sample dates
tape 8 : spray dates
tape 9 : rain dates
tape 17: nrmove

Output files

tape 14: pest dist

The values of spray distribution used to write the output file (tape 14) pestdist are the average spray distributions for each year.

To calculate drift for the forward model, a regression was run on drift vs. windspeed. Windspeeds for each spraydate were estimated from Grand Rapids weather data, and drifts used were the proportion drift of a spray calculated by SPRDIST. The regression yielded

$$\text{DRIFT} = 0.03409 * WS_{GR} + 0.09314$$

Penetration Subroutine

For litter: The following calculations are performed by the penetration subroutine:

(1) $$\frac{dP_L}{dt} = \text{Kin } D_2 - KP_L \, P_L(t) + K_{iPL}T(0)$$

where:

$$\frac{dP_L}{dt} = \text{Rate of change in penetrated residues}$$

Kin = Penetration rate of D_L, litter DSL residues
KP_L = Attenuation rate of P_L, litter Pen residues
K_{iPL} = Instantaneous penetration of total residues applied (Day 0)
D_L = Dislodgeable residue in layer L
P_L = Penetrated residue in layer L

and

(2) $$\frac{dD_L}{dt} = -Kin\ D_i(t) - Kd_L\ D_L(t) - K_{mo} m_L(t) + \Sigma\ K_{ei}\ D_i(t)$$

were: $\frac{dD_L}{dt}$ = Rate of change of litter DSL residues
Kd_L = Attenuation rate (other than penetration) of D_L, DSL residues
K_{mo} = Rate of movement out of DSL residues (D_L)
ΣK_{ti} = D_i (t) = Sum of DSL residues transfered from above layers to Layer L

(3) $$\Sigma K_{ti}\ D_i(t) = K_{t\ LV}\ D_{LV}(t) + K_{tg}\ D_g(t)$$

For moss:

(4) $$\Sigma K_{ti}\ D_i(t) = K_{tLV}\ D_{LV}(t) + K_{tg}\ D_g(t) + K_{tL}\ D_L(t)$$

where:

K_{tLV} = Transfer rate of DSL residues in tree, D_{LV}, to litter (a separate K_{tLV} for transfer to alley litter and canopy litter)
K_{tg} = Transfer rate of grass DSL residues, D_{gl} to litter
K_{tL} = Transfer rate of litter DSL residues

K_{PL} in eq. 1 was estimated by making the following assumptions:

a. The observed atteruation of litter DSL residues is the sum of penetration, degradation and volatilization rates.
b. For residues deposited on the grass, there is little penetration during the spray period above that which is initially penetrates (K_{ipg} T(k) as compared to DSL residue penetration (K_{in}) into litter and moss during the spray period and therefore observed attenuation rate for grass DSL residues is the sum of degradation and volatilization only.
c. Degradation and volatilization of litter and moss DSL residues is similar to grass DSL residues.

NOTE: Degradation of PEN residues may be quite different due to plant uptake and metabolism.

d. Then the penetration rate, K_{in}, for litter or moss can be estimated from the difference between the litter (or moss) DSL residue attenuation rate (from ADAPT) and the grass DSL residue attenuation rate (from ADAPT).

The following K_{in}'s were determine for litter and moss

	Canopy	Alley
Litter	.026	.055
Moss	.227	.498

K_{iPL} was estimated from the observed ratio of penetrated to total residues for samples taken 4 hrs. following application (day 0). (Use matched pairs on spray dates).

K_{iPL} = .297 (78)

K_{iPm} = .214 (78 data only) .232 (76 + 78 data)

$$P(t) = P(t-1)\ (1-Kp) + (DSL_L(t-1)\ .\ (1-k_{in}))$$

For $P(t-1) = P(t_o)$, $P(t-1) = K_{ip}\ .\ DSL_L(o)$

NOTE: Penetrated residues on day t = penetrated residues on day t-1 times daily degradation rate of DSL residues present on day t-1 times daily penetration rate.
ex: (for litter)

$$DSL_L(t) = DSL_L\ (t-1) \cdot (1-Kd) - DSL_L\ (t-1) \cdot (1-K_{mo}) + DSL_{LV}(t-1) \cdot (1-K_{tLV}) + DSL_g\ (t-1) \cdot (1-K_{tg})$$

NOTE: Litter DSL residues at day t = litter DSL residues on day t-1 times daily deg rate - litter DSL res on Day t-1 times daily transfer rate + grass DSL res on day t-1 times daily transfer rate.

Subroutine Allyest

Allyest uses target proportions to estimate missing alley samples from alley samples that are present. If all alleys (1, 2, and 3) are missing it cannot estimate anything. Therefore, while this routine is operating we have either all three alley values (if one or two different alley regions are missing we estimate what's missing from what is present) or we have no alley data at all for a given plot and day.

To fill in missing data we set the missing value equal to the value present weighted by the ratio of alley area for value present to alley area of missing value and weighted by the ratio of target proportion of missing alley to target proportion of alley present.

Next, the 3 alley region averages are averaged across alley regions weighted by alley region area and stored into alley region #3 (which now represents all alley regions).

The POEM Model User's Guide

Introduction

The Pesticide Orchard Ecosystem Model was constructed for two major reasons:

(1) to assist in presenting the results of a study of the fate of a particular compound under field conditions and its effects on some significant organisms using laboratory and field data, and

(2) to allow users to explore the implications of changes in the model's parameters on the model outcomes (both fate and effects), including limited extrapolation to other compounds and/or field conditions.

The various submodels included in POEM and the methods used to parameterize them are described in the body of this report and in a series of publications. This guide is intended only to supplement them, as an aid to persons desiring to run the associated computer programs. No explanation is offered here of the methods used to derive the parameters included as default values, nor is there any presentation of results (see the body of the report).

POEM is a modular FORTRAN IV program, composed of many subunits which may be invoked or left idle during any particular run. In general, POEM units not needed should be "turned off" to minimize computer costs. POEM may be used to explore the behavior of the fate model using "average" values independent of temperature and relative humidity, or may be instructed to re-calculate certain parameters daily based on environmental conditions.

Many of POEM's parameters for azinphosmethyl may be altered in order to incorporate new data or determine the effects of such changes on pesticide distribution or effects on the modeled populations. Other alterations allow the user to enter information to simulate a different compound. Weather data may be entered by the user, or the program may be used to generate simulated weather data. The user must supply pesticide application information, unless the default regime used in our field studies is desired.

In its simplest use, POEM can be used with minimal input data and will produce predictions of the pesticide distributions and populations to be found in our study orchard under our measured environmental conditions from 1976-1978. POEM produces output files suitable for plotting, and two plotting programs are included (one for pesticide residues, one for populations). Alteration of compound characteristics, weather data, or process-specific parameters may require the user to enter much larger amounts of data, although it is relatively easy and often enlightening to explore the effects of changing one or a few parameters at a time.

The next few sections describe the general nature of the units in the fate model, followed by directions for and examples of reparameterization. A brief description of the organism submodels is included under Organism Graphs; however, the automatic alteration of organism model parameters has not yet been completely implemented. See the relevant sections of the body of the report for more information.

Attenuation of Pesticide

The attenuation model simulates attenuation, other than penetration, in the various compartments. Each compartment has an attenuation proportion--the proportion of pesticide within or entering that compartment during one day that is attenuated (see below) from that compartment during a one day time step at standard conditions. The standard conditions approximate the average of those prevailing during collection of the field data used to parameterize this model. These conditions are:

1) environmental conditions
    - soil PH = 7.0
    - % organic matter of soil = 6%
2) compound properties
    - molecular wt. = 317
    - vapor pressure = 10^{-7} atm.

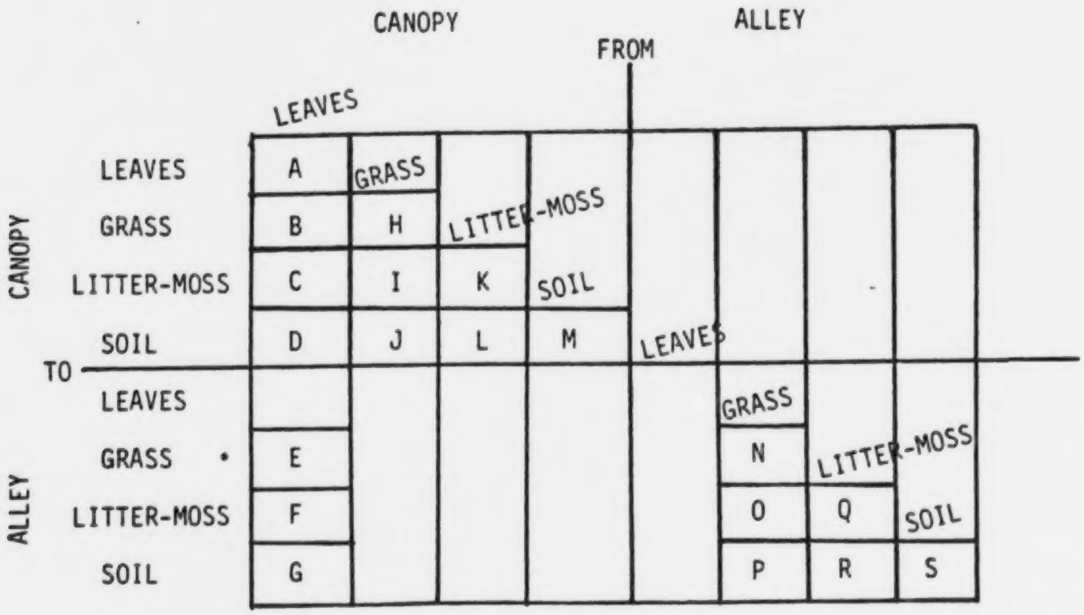
Each compartment's attenuation proportion is further broken down into 5 attenuation processes: hydrolysis, photolysis, oxidation, volatilization, and microbial degradation. Therefore each compartment has an attenuation proportion for each of the five attenuation processes. The sum of the attenuation proportions for each process of a given compartment is equal to the overall attenuation proportion for that compartment.

The user has the option of using the overall attenuation proportions for each compartment directly as the proportion of pesticide lost each day due to attenuation. Or the user may allow individual attenuation proportions of the attenuation process to vary with environmental conditions. Thus, the sum of the attenuation proportions of the five attenuation processes over a compartment, which yields the day's overall attenuation proportion for that compartment will vary daily with environmental conditions.

In addition, the user may alter certain default parameters to represent properties of a compound other than azinphosmethyl, the compound used in the field studies. The overall attenuation proportions, whether constant or varied with daily conditions, are applied each day and represent the proportions of pesticide attenuated daily from each compartment.

Non-rainfall Movement of Pesticide

Subroutine Nonrain simulates the daily movement of pesticide within the orchard independent of rainfall during the period (i.e., it is applied every day). It operates conservatively; that is, it moves residues without any losses, which must therefore be accounted for elsewhere in the model (see Attenuation description in previous section). It operates only on dislodgeable residues, except that residues entering the soil layers are considered to be "penetrated residues." Pesticide is assumed to move only from a higher layer to lower layers, and pesticide moving to the alley region from the canopy region may only come from the canopy leaves compartment. The order of layers from highest layer to lowest layer is leaves, grass, litter-moss, and soil. The pesticide is moved via a lower triangular matrix "NRMOVE".


CANOPY
ALLEY
FROM
TO
LEAVES
GRASS
LITTER-MOSS
SOIL
CANOPY
LEAVES
GRASS
LITTER-MOSS
SOIL
ALLEY
LEAVES
GRASS
LITTER-MOSS
SOIL
A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
P
Q
R
S

Each entry in the matrix represents a proportion of the total amount of dislodgeable pesticide residue present on a given day that moves from one compartment to another or (for diagonal entries) that remains in the same compartment. The latter (diagonal) entries in the matrix are A,H,K,M,N,Q,S. A single column in the matrix represents the movement from an individual compartment over a one day time step. Being proportions of the total amount of what was in a compartment, all entries of any column in the matrix must sum to one. Since there is only one entry for each of the canopy soil and alley soil compartments, entry M=1.0 and entry S=1.0 by the definition that the columns must sum to one (implying that pesticide undergoes no non-rain-induced movement out of soil layers).

For example:

B is the proportion of pesticide moving from the canopy leaves compartment to the canopy grass compartment during a one day time step. H is the proportion of the canopy grass compartment that remains in the canopy grass compartment during a one day time step. Thus the entire amount of dislodgeable pesticide in the canopy grass on day t+1 (excluding attenuation) is equal to the B times the amount of dislodgeable pesticide in the canopy leaves on day t plus H times the amount of dislodgeable pesticide in the canopy grass on day t:

$$\mathrm{CanGr}(t+1) = B \cdot \mathrm{CanLvs}(t) + H \cdot \mathrm{CanGr}(t)$$

The absolute amount of pesticide for any compartment of day t+1 can be represented by the sum of each entry in that compartment's "TO" row of the matrix, multiplied by the absolute amount of pesticide on day t in the appropriate compartment (neglecting attenuation and rainfall-induced movement).

It is important that pesticide values be converted from their normal form of $\mu g/cm^2$ ground area to an absolute amount (in μg.) of pesticide when applying the matrix. This is because canopy and alley regions do not necessarily have the same ground areas and because the canopy leaves column may move pesticide from the canopy region into the alley region. In order for the system to be conservative, the pesticide values in $\mu g/cm^2$ ground area are converted to amount of pesticide in μg. before the matrix is applied and converted back to $\mu g/cm^2$ ground area afterwards.

The non-rain movement matrix is applied every day regardless of rainfall. It represents the daily movement, other than by rainfall, of the pesticide within the orchard system.

The default values of the non-rain movement matrix are those parameterized from field data.

It is possible to change the matrix during reparameterization in a variety of ways as described under the Movement Parameters category of the Reparameterization section.

Movement of Pesticide Due to Rainfall

Subroutine Rain simulates movement of pesticide within the system due to rainfall. There are two rainfall matrices that have the same properties and are applied similarly to the non-rain movement matrix. One of the two matrices is applied on each day of measurable rainfall. One represents light rainfall movement, the other represents heavy rainfall movement. A heavy rain is classified as greater than or equal to 10mm on a given day. Less than 10mm rain is considered a light rain. Rainfall movement is defined as additional movement beyond the nonrain movement extracted daily.

It is also possible to change either or both rainfall matrices from their default conditions. See Movement Parameters under the Reparameterization section for further details.

Application of Pesticide

Subroutine Sprayer simulates the application of pesticide to the orchard. The total amount of pesticide (in μg.) that reaches the orchard is first calculated. It is equal to the amount applied (in Kg./Ha.) multiplied times the area of the orchard (in Ha.) times a Kilogram to microgram conversion factor (10^{-9}) times the compound formulation fraction times the proportion of pesticide that doesn't drift away from the orchard site. This yields the absolute amount of pesticide (in micrograms) that reached the orchard site. The proportion of drift is calculated based on the wind speed. Once the absolute amount of pesticide reaching the orchard is known, it is divided among the compartments using a spray distribution vector, "PDIST", where an entry represents the proportion of pesticide going to a specific compartment from the total amount of pesticide reaching the orchard. Thus, the sum of all entries in the spray distribution vector is equal to one.

However, some of the pesticide that reaches a compartment becomes penetrated residue. The spray distribution only gives the amount of pesticide that reaches a compartment. The pesticide that reaches each compartment, except for soil layers (all pesticide in the soil is assumed penetrated), is further divided into dislodgeable and penetrated residues. Finally, units are converted from μg to μg/cm^2 by dividing the absolute amount of pesticide in each layer by the area of its region (canopy or alley).

The spray distribution vector may be altered to a new form in the Movement Parameters section of the Reparameterization section. Likewise, initial penetrations of a layer may also be changed in the Penetration Parameters section of the Reparameterization section.

Penetrated Residue Attenuation

Subroutine Pentrat simulates the penetration of dislodgeable residues to become penetrated residues and the attenuation of penetrated residues. There is a daily penetration rate representing the proportion of dislodgeable residue that penetrates each day, and a penetrated residue attenuation proportion representing the proportion of penetrated residue that attenuates daily. Each of the proportions is applied daily regardless of spraying. Also, the proportions may be changed in the Penetration Parameters category of Reparameterization.

Mowing of the Orchard

Subroutine Mower simulates mowing of the orchard. It moves a proportion of pesticide from the grass layer to the litter-moss layer. The proportion of grass moved, "PGRASM", may be changed to any proportion (0.0 to 1.0) in the movement parameters category during reparameterization of the model. The default value of "PGRASM" for the field site is 0.0. The proportion of the grass layer moving to the litter-moss layer is assumed linear with the proportion of pesticide moving from the grass layer to the litter-moss layer because of mowing.

The maximum number of mow dates allowed for any one season is ten. The user may select any dates he wishes. The mow dates for a season are entered just before the beginning of that season.

Leaf Growth of Trees

Subroutine Trees computes the tree interception index "TII", a value which converts the ground area under the canopy region to tree surface area (including leaves). Growth in surface area is driven by degree days until petal fall (1100 degree days, base 43°F), and then is considered linear until 56 days after petal fall at which time the TII has reached maximum.

Running the Model

The user has many options in running POEM--some of these options call for the use of pre-stored files of weather data. For example, if the weather simulator is not used, POEM will attach a file called WTHRSTATSNEW, which should contain the weather information you wish to use (a file with 3 years of data for Grand Rapids, MI is included). Similarly, if the soil moisture model is not used, POEM will seek soil moisture data from a file called PWSMOIST2. (On non-MSU systems, subroutine PARMINT should be altered to conform to local procedures for accessing these files. For more information, see section entitled "Attaching Tapes".)

Output from POEM is available in two forms--printed tables and graphs. Graphical output is provided by specifying to POEM that graphical output is desired. Two types of graphs are available: pesticide levels versus time and population levels versus time. Pesticide level graphs are obtained by turning on option (14) (see below) and post-processing using program DATAPLT (available on the MSU CYBER as ORCHARDCALPLOT6 for CALCOMP plotter output or ORCHARDTEKPLOTB for Tektronix terminal display via PLOT-10 subroutines). Population graphs are produced from files generated whenever the organism submodel (option 1) is on, using program ORGPLOT (again, available on MSU's CYBER in CALCOMP and Tektronix versions). For more information on the plotting programs, see section "Producing Graphs" below.

Printed output to display pesticide levels and/or the current rates of pesticide movement and attenuation are available in POEM as described below. Printed output from organism models is not specifically provided for, but is available by listing the plotting files generated by POEM.

Options and submodels turned on by default as execution begins are listed, followed by a list of other available options. The user then has the opportunity to turn off any options that are on by default or turn on any of the options that are off by default, in response to queries from the program. The submodels that each option represents are:

option 1) Organism submodels. "1" for any one or combination of the 4 organism models provided (isopod, collembolan, spider, or earthworm); further options will be presented, or "2" otherwise.

option 2) Mower submodel. "1" for periodic mowing of the orchard each season. The maximum number of mows allowed each year is 10. The mow dates for a given year are entered at the start of that year.

option 3) Attenuation submodel. "1" to use attenuation as a lumped process or to use any of the attenuation submodels (microbial degradation, hydrolysis, photolysis, volatilization, oxidation); "2" to bypass pesticide attenuation calculations.

(Any further reparameterization concerning these attenuation processes is done in the general category of attenuation parameters, below.)

option 4) Weather submodel. "1" to turn on simulated weather. To allow true recorded weather conditions, the weather simulator must be turned off. In that case, the recorded weather must be provided on tape 4 and must contain the following conditions for each day in a required format:

- minimum and maximum air temperature (^oF)
- minimum and maximum percent rel. humidity
- average wind speed (mi/hr), and total rain (mm)

See Attaching Tapes for more information.

option 5) Nonrain Movement Submodel. "1" to select daily movement of pesticide; "2" suppresses movement except on days with rain.

option 6) Sprayer Submodel. "1" for periodic spraying of pesticide during the season. The maximum number of sprays each year is ten. The spray dates and spray amounts for a given year are entered at the start of that year, unless default dates and amounts are desired.

option 7) Rainfall submodel. "1" for additional pesticide movement (other than daily nonrain movement) due to rainfall if rainfall is present; "2" suppresses pesticide movement in response to rainfall.

option 8) Penetration submodel. "1" for pesticide penetration submodel. Any further reparameterization concerning penetration (see text) is found in the general category of penetration parameters. If option 8 is off, the proportions of daily penetration are assumed to be accounted for by other attenuation processes, provided option 3 is turned on.

option 9) Soil moisture model. "1" for simulated soil moisture based on amount of rainfall. True recorded soil moisture values may be provided, but the simulated soil moisture model must be turned off. If the soil moisture model is off, recorded soil moistures must be provided on tape 9. See Attaching Tapes for more details.

option 10) Tree growth submodel. "1" for daily leaf and tree growth based on degree days.

option 11) Movement Matrix printout. Provides daily printout of a matrix which combines the non-rain movement matrix with the attenuation matrix. This matrix captures the net effects of the environment-dependent processes acting on the pesticide, under non-rainfall conditions, as represented by the model. Beginning and ending dates for printout of this matrix for a given year are entered at the start of that year. This option is provided to see movement and attenuation that vary daily with environmental conditions, as influenced by compound properties.

option 12) Soil Transportation model. "1" selects more detailed model of soil layer.

option 13) Pesticide Output. "1" selects printing periodic pesticide values; mow, rain, and spray date flags are also printed.

option 14) Plotting Output. "1" writes formatted file of pesticide values to tape 1, file of spray dates to tape 2, and file of rain dates and amounts to tape 3 for plotting package.
See Plotting Package for more details.

option 15) Event dates. "1" allows the user to enter dates of events of sprays and mows. If this option is off, event dates are those from field data used to parameterize this program.

option 16) Variable attenuation. "1" allows daily attenuation proportions of the various attenuation processes to vary daily with environmental conditions, and to reflect compound properties other than those of azinphosmethyl. If option 16 is off, attenuation proportions will be identical each day, and based on the measured values for azinphosmethyl.

If the user selects the organism model option, he must then select one or any combination of the four organism models (isopod, collembolan, spider, earthworm). He is asked individually for each organism model to be turned on or off.

If organism models are desired without the effects of pesticide, then the sprayer (option 6) should be off. Therefore, no pesticide is sprayed to the orchard.

It is suggested that if the sprayer option is off, then options 2, 3, 5, 7, 8, 10, 11, 12, 13, 14 also be off since all of these submodel options pertain to movement or output of pesticide and no pesticide can be present without the sprayer submodel. Additionally, option 16 deals with attenuation and has no effect unless option 3 is on.

Sample

```
THE FOLLOWING OPTIONS ARE ON BY DEFAULT

        ORGANISM SUBMODEL
        ATTENUATION SUBMODEL
        NON-RAIN MOVEMENT SUBMODEL
        PESTICIDE APPLICATION SUBMODEL
        RAINFALL MOVEMENT SUBMODEL
        PENETRATION SUBMODEL
        WRITE FILES FOR PLOTTING PACKAGE
        VARIABLE   ATTENUATION

OTHER AVAILABLE OPTIONS ARE

        MOWER SUBMODEL
        WEATHER SIMULATOR
        SOIL MOISTURE SIMULATOR
        LEAF GROWTH SUBMODEL
        MOVEMENT MATRIX DAILY OUTPUT
        SOIL TRANSPORTATION SUBMODEL
        PESTICIDE PRINTOUT
        NON-DEFAULT EVENT DATES -SPRAYS,MOWS,ETC

DO YOU WISH TO TURN ON OR OFF ANY OPTIONS?
        (1) YES  (2) NO 1

ENTER A VALUE FOR EACH OPTION
        (1) FOR OPTION ON  (2) FOR OPTION OFF
    OPTION  1     ORGANISM SUBMODEL 2
    OPTION  2     MOWER SUBMODEL 1
    OPTION  3     ATTENUATION SUBMODEL 1
    OPTION  4     WEATHER SIMULATOR 2
    OPTION  5     NON-RAIN MOVEMENT SUBMODEL 1
    OPTION  6     PESTICIDE APPLICATION SUBMODEL 1
    OPTION  7     RAINFALL MOVEMENT SUBMODEL 1
    OPTION  8     PENETRATION SUBMODEL 1
    OPTION  9     SOIL MOISTURE SIMULATOR 2
    OPTION 10     LEAF GROWTH SUBMODEL 2
    OPTION 11     MOVEMENT MATRIX DAILY OUTPUT 1
    OPTION 12     SOIL TRANSPORTATION SUBMODEL 2
    OPTION 13     PESTICIDE PRINTOUT 1
    OPTION 14     WRITE FILES FOR PLOTTING PACKAGE 2
    OPTION 15     NON-DEFAULT EVENT DATES -SPRAYS,MOWS,ETC 1
    OPTION 16     VARIABLE   ATTENUATION 1
```

After the correct submodel choices have been selected, other simulation parameters are entered.

First, the user is asked how many years to run the model. The maximum number of years is ten, and the model must be run at least one year.

Second, if the user has chosen option 13 of the on-off vector, he is asked how often in days he would like pesticide values printed to output. Selecting pesticide output (option 13) automatically causes printing of mow, spray, and rain dates where they are appropriate, along with pesticide values on spray dates. If the user inputs "10" for the pesticide value printout increment, pesticide values will also be printed to output every ten days.

Example

```
HOW MANY YEARS DO YOU WISH TO SIMULATE( ONE TO TEN YEARS)1
HOW OFTEN (IN DAYS) WOULD YOU LIKE PESTICIDE VALUES PRINTED TO OUTPUT 1
```

Reparameterization

General Categories of Reparameterization

Reparameterization is divided into five general categories. If the user chooses to reparameterize, he must select one of these general categories. The five categories are:

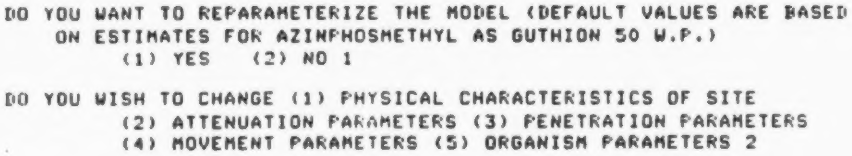
1) physical site characteristics
    - basic site characteristics (areas, # trees, % alley and canopy area)
    - site characteristics needed for soil moisture model (altitude, latitude, soil moisture, field capacity, etc.)
2) attenuation parameters
    - attenuation proportions
    - environmental properties (soil pH, % organic matter)
    - coefficients of equations dependent on environmental conditions
    - compound properties
3) penetration parameters
    - initial penetration rates
    - daily penetration rates
    - penetrated residue attenuation rates
4) pesticide movement parameters
    - spray distribution
    - non-rain movement matrix
    - rainfall movement matrix
    - proportion of grass mowed

5) organism parameters

   - isopod parameters
   - collembolan parameters
   - spider parameters
   - earthworm parameters

When entering options to select from, the user inputs the number of the option he wishes. When the user is asked for more than one input value for a given line, each of the values must be separated by blank(s) or a comma.

<u>Example</u>



```
DO YOU WANT TO REPARAMETERIZE THE MODEL (DEFAULT VALUES ARE BASED
    ON ESTIMATES FOR AZINPHOSMETHYL AS GUTHION 50 W.P.)
        (1) YES   (2) NO 1

DO YOU WISH TO CHANGE (1) PHYSICAL CHARACTERISTICS OF SITE
        (2) ATTENUATION PARAMETERS (3) PENETRATION PARAMETERS
        (4) MOVEMENT PARAMETERS (5) ORGANISM PARAMETERS 2
```

After a general category is selected and reparameterization is completed for that category, the user will be asked if he wishes to continue reparameterization. If he selects "NO", execution will begin. However, if he selects "YES", he may select any general category originally offered including the one just completed.

All dates asked for should be entered in a Julian date format (a number from 1 to 365 representing which day of the year it is; i.e., February 1 would be day 32 because it is the 32nd day of the year). Leap years are ignored, so day 365 is the maximum date for any year.

1. Physical Characteristics of Orchard Site

This category first asks for basic physical characteristics defining the site. Values for total area, of site, amount of site that is canopy region (remainder is alley region), and the number of trees in the site requested one at a time. When asking for one of these values, the model will list the default condition. Default conditions are those of the field study site for which the model was originally parameterized.

If the soil moisture submodel (option 9) is on, additional physical characteristics (initial percent soil moisture, field capacity for soil moisture, altitude of site, latitude of site, etc.) necessary for the soil moisture submodel are asked for in the same manner as the other physical site characteristics.

Example

```
DO YOU WISH TO CHANGE (1) PHYSICAL CHARACTERISTICS OF SITE
          (2) ATTENUATION PARAMETERS (3) PENETRATION PARAMETERS
          (4) MOVEMENT PARAMETERS (5) ORGANISM PARAMETERS 1

HOW MANY HECTARES OF GROUND AREA WOULD YOU LIKE YOUR ORCHARD:
          (CURRENT AREA = .0812 HA.) 1.0

HOW MUCH (IN HECTARES) OF THE 1.0000 HECTARE ORCHARD WILL BE CANOPY REGION
     (CURRENT CANOPY AREA = .0302 HA.)
     (THE REMAINDER OF AREA IS CONSIDERED ALLEY REGION) .40

HOW MANY TREES ARE IN THIS ORCHARD?
     (CURRENT NUMBER OF TREES = 60)800

ENTER PERCENT W/W SOIL MOISTURE CONTENT AT THE FIRST DAY
          (CURRENT INITIAL SOIL MOISTURE CONTENT = 30.00 PERCENT W/W) 25.

ENTER PERCENT W/W SOIL MOISTURE FIELD CAPACITY
          (CURRENT FIELD CAPACITY = 60.00 PERCENT W/W) 60

ENTER BULK DENSITY (IN GM.CM**3) OF SOIL
          (CURRENT BULK DENSITY = 1.500 GM./CM**3) 1.4

ENTER ALTITUDE (IN METERS) OF SITE
          (CURRENT ALTITUDE = 200.000 M) 240
```

```
ENTER LATITUDE OF SITE
        (CURRENT LATITUDE =  40.00 DEGREES) 40.

ENTER DIFFERENCE IN MEAN AIR TEMPERATURES (DEGREES C) BETWEEN
        WARMEST AND COOLEST MONTHS OF THE YEAR
        (CURRENT DIFFERENCE =  27.80 C) 28.

ENTER EVAPOTRANSPIRATION FACTOR DUE TO FLORA
        (CURRENT EVAPOTRANSPIRATION FACTOR =  1.00) 1.00

ANY MORE REPARAMETERIZATION? (1) YES  (2) NO 2
```

2. Attenuation Parameters

The attenuation parameters are divided into four basic groups: 1) lumped attenuation parameters, used only if option (16) is off, yielding constant daily rates of attenuation; 2) daily attenuation proportions for various processes (microbial degradation, volatilization, oxidation, hydrolysis, and photolysis) for the various regions and layers; 3) attenuation parameters describing effects of environmental conditions; and 4) attenuation parameters describing compound properties different from those of azinphosmethyl.

When the attenuation parameters category of reparameterization is selected, the current daily attenuation proportions at standard conditions are displayed. The standard conditions are approximately the average of the conditions obtained during the collection of the field data used to parameterize the model. These conditions are:

1) environmental conditions
    - soil pH = 7.0
    - % organic matter of soil = 6%
2) compound properties
    - molecular wt. = 317
    - vapor pressure = 10^{-7} atm.

The daily attenuation proportion matrix represents proportions of the amount of pesticide in each region and layer that is attenuated under the above standard conditions during one day.

If option (16) is off, and after the attenuation proportion matrix is displayed, the user may change any number of entries in the matrix one at a time, display the new matrix after some entries have been changed, or exit the daily attenuation proportion matrix change mode once he is satisfied with attenuation proportions at standard conditions.

Example

```
CURRENT ATTENUATION PROPORTIONS AT STANDARD CONDITIONS ARE:

                  LEAVES          GRASS          LITTER            SOIL
 CANOPY            0.0487          0.0412          0.0412          0.0790
 ALLEY             0.0000          0.0670          0.0670          0.0790

WOULD YOU LIKE TO (1) CHANGE AN ENTRY IN THE STANDARD CONDITION ATTENUATION
          MATRIX
          (2) SEE CURRENT DAILY ATTENUATION PROPORTIONS
          (3) EXIT ATTENUATION PROPORTION CHANGE MODE 1

ENTER REGION (1) CANOPY (2) ALLEY
     LAYER (1) LEAVES (2) GRASS (3) LITTER-MOSS (4) SOIL
     ATTENUATION PROPORTION (VALUE FROM 0.0 TO 1.0) 1 2 .050

WOULD YOU LIKE TO (1) CHANGE AN ENTRY IN THE STANDARD CONDITION ATTENUATION
          MATRIX
          (2) SEE CURRENT DAILY ATTENUATION PROPORTIONS
          (3) EXIT ATTENUATION PROPORTION CHANGE MODE 2

CURRENT ATTENUATION PROPORTIONS AT STANDARD CONDITIONS ARE:

                  LEAVES          GRASS          LITTER            SOIL
 CANOPY            0.0487          0.0500          0.0412          0.0790
 ALLEY             0.0000          0.0670          0.0670          0.0790

WOULD YOU LIKE TO (1) CHANGE AN ENTRY IN THE STANDARD CONDITION ATTENUATION
          MATRIX
          (2) SEE CURRENT DAILY ATTENUATION PROPORTIONS
          (3) EXIT ATTENUATION PROPORTION CHANGE MODE 3

ANY MORE REPARAMETERIZATION? (1) YES (2) NO 2
```

If option (16) is on, then the above matrix serves only to show standard conditions totals for daily attenuation. The matrix used will be calculated daily, based on the environmental conditions. The daily attenuation proportion matrix is further subdivided, into 5 components. Each entry in the new matrix represents one of five attenuation processes (hydrolysis, photolysis, oxidation, microbial degradation, volatilization). This new daily attenuation proportion matrix, broken down by region, layer, and attenuation processes, is displayed. Its entries represent daily proportions attenuated under standard conditions, and the daily rates actually used will be these entries multiplied by environmentally-dependent factors, described below.

The user then has the option to change this new matrix. If he decides to change the matrix he has the option to change a single entry in the matrix, the contribution of an entire process (a row in the matrix), or each process for a given region and layer (a column in the matrix). After the user makes any type of change in either of the two previous matrices (overall daily attenuation proportion matrix for a given region and layer, and the same matrix also divided by contributions of different attenuation processes), the user again has the option to change the matrix in the manner just described or keep it as it is.

<u>Example</u>

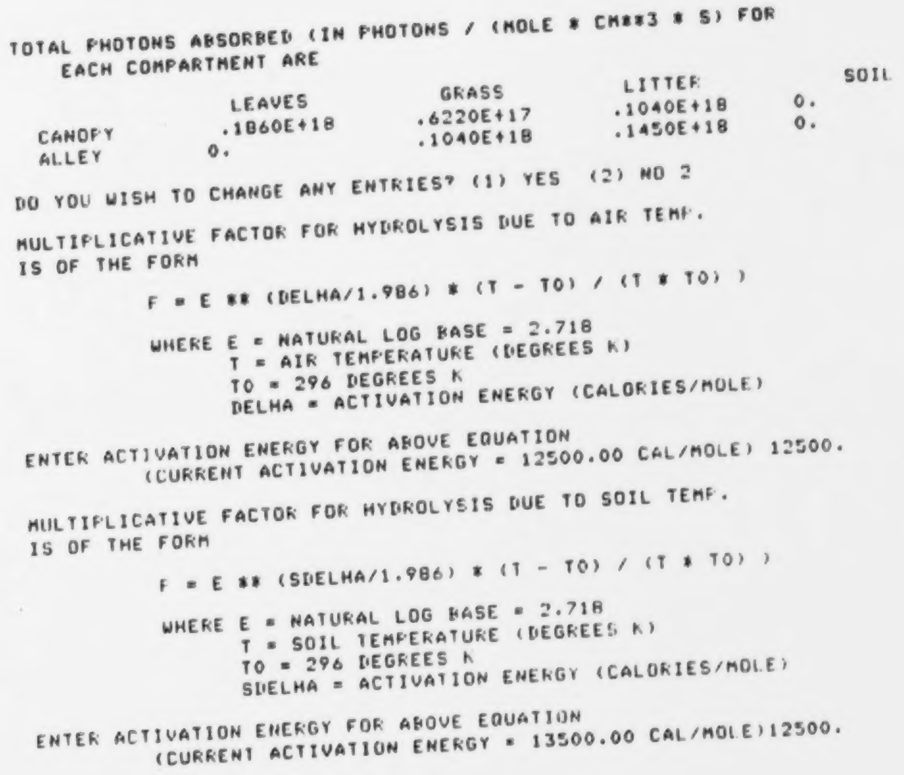
```
CURRENT OVERALL ATTENUATION PROPORTIONS AT STANDARD CONDITIONS ARE:

                 LEAVES          GRASS          LITTER          SOIL
  CANOPY          .0487          .0412          .0412          .0790
  ALLEY          0.0000          .0670          .0670          .0790

THE CONTRIBUTION OF INDIVIDUAL PROCESSES TO OVERALL ATTENUATION
AT STANDARD CONDITIONS ARE:

                                        MATRIX AP
                     C 1     C 2     C 3     C 4     A 1     A 2     A 3     A 4
MICROBIAL DEG.      0.000   0.000    .010    .070   0.000   0.000    .017    .070
HYDROLYSIS           .012    .012    .015    .009   0.000    .019    .025    .009
PHOTOLYSIS           .018    .006    .003   0.000   0.000    .010    .004   0.000
VOLATILIZATION       .019    .024    .013   0.000   0.000    .038    .021   0.000
OXIDATION           0.000   0.000   0.000   0.000   0.000   0.000   0.000   0.000

WOULD YOU LIKE TO CHANGE THE ATTENUATION PROPORTIONS AT STANDARD
CONDITIONS ALLOCATED TO DIFFERENT TYPES OF ATTENUATION
        (1) YES  (2) NO 1
```

```
WOULD YOU LIKE TO CHANGE (1) A SINGLE ENTRY IN THE MATRIX AP
         (2) A ROW IN THE MATRIX
         (3) A COLUMN IN THE MATRIX 1

ENTER 4 NUMBERS
FIRST  NUMBER- REGION (1) CANOPY  (2) ALLEY
SCEOND NUMBER- LAYER  (1) LEAVES (2) GRASS (3) LITTER-MOSS (4) SOIL
THIRD  NUMBER- PROCESS (1) MICROBIAL DEG. (2) HYDROLYSIS (3) PHOTOLYSIS
         (4) VOLATILIZATION (5) OXIDATION
FOURTH NUMBER- ATTENUATION PROPORTION FOR THE REGION, LAYER, PROCESS YOU
         HAVE SELECTED (PROPORTION MUST BE FROM 0.0 TO 1.0) 1 4 1 .060

CURRENT OVERALL ATTENUATION PROPORTIONS AT STANDARD CONDITIONS ARE:

                 LEAVES          GRASS           LITTER           SOIL
  CANOPY          .0487           .0412           .0412           .0690
  ALLEY          0.0000           .0670           .0670           .0790

THE CONTRIBUTION OF INDIVIDUAL PROCESSES TO OVERALL ATTENUATION
AT STANDARD CONDITIONS ARE:

                                         MATRIX AP
                           C 1    C 2    C 3    C 4    A 1    A 2    A 3    A 4
MICROBIAL DEG.           0.000  0.000   .010   .060  0.000  0.000   .017   .070
HYDROLYSIS                .012   .012   .015   .009  0.000   .019   .025   .009
PHOTOLYSIS                .018   .006   .003  0.000  0.000   .010   .004  0.000
VOLATILIZATION            .019   .024   .013  0.000  0.000   .038   .021  0.000
OXIDATION                0.000  0.000  0.000  0.000  0.000  0.000  0.000  0.000

WOULD YOU LIKE TO CHANGE THE ATTENUATION PROPORTIONS AT STANDARD
CONDITIONS ALLOCATED TO DIFFERENT TYPES OF ATTENUATION
         (1) YES  (2) NO 2
```

Once the daily standard attenuation proportions are set, the user has the option to change environmental properties of the site or compound properties. He is given standard conditions of necessary environmental and compound properties such as soil pH, % soil organic matter, vapor pressure, etc. and asked to input the value of the property.

Example

```
DO YOU WISH TO CHANGE ENVIRONMENTAL PROPERTIES OR COMPOUND PROPERTIES
        (1) YES  (2) NO 1

ENTER SOIL PH VALUE (CURRENT PH = 7.000) 6.5

ENTER PERCENT ORGANIC MATTER OF SOIL (CURRENT
         PERCENT ORGANIC MATTER = 6.000) 6.0

MULTIPLICATIVE FACTOR FOR VOLATILIZATION IS OF THE FORM

         F = (VP * MW**0.5) / (STDVP * STDMW**0.5)

         WHERE VP = VAPOR PRESSURE OF CURRENT COMPOUND
               MW = MOLECULAR WEIGHT OF CURRENT COMPOUND
               STDVP = VAPOR PRESSURE OF STANDARD COMPOUND (AZINPHOSMETHYL)
                     = .0000001 ATM.
               STDMW = MOLECULAR WEIGHT OF STANDARD COMPOUND (AZINPHOSMETHYL)
                     = 317

ENTER COMPOUND VAPOR PRESSURE( IN ATM.)
         (STANDARD COMPOUND VAPOR PRESSURE =  .0000001000 ATM.) .0000001

ENTER COMPOUND MOLECULAR WEIGHT (STANDARD COMPOUND MOLECULAR WEIGHT = 317) 317

ENTER COMPOUND FORMULATION (IN PERCENT)
         (STANDARD COMPOUND FORMULATION =  50.00PERCENT WETTABLE POWDER) 50.

MULTIPLICATIVE FACTOR FOR PHOTOLYSIS IS OF THE FORM

         F = (2.303/CONST) * PHI * SIGMA * AQS * DIURN / DEF

         WHERE CONST = CONVERSION CONSTANT = 6.02 * 10**20
               PHI = QUANTUM YIELD
               SIGMA = TOTAL PHOTONS ADSORBED (DIFFERENT FOR EACH COMPARTMENT)
               AQS = A MULTIPLICATIVE FACTOR TO ALLOW FOR NATURALLY OCCURRING
                     LIGHT ABSORBERS, SENSITIZERS, AND QUENCHERS
               DIURN = DIURNAL CONVERSION FACTOR TO LOSS RATE AT PEAK
                         SUNLIGHT INTENSITY TO DAILY PROPORTIONAL LOSS
                     = 2.52 * 10**4
               DEF = ATTENUATION PROPORTION ENTRY FOR PHOTOLYSIS (DIFFERENT
                     FOR EACH COMPARTMENT)

ENTER QUANTUM YIELD (IN MOLES CONVERTED PER PHOTON ABSORBED)
         (CURRENT QUANTUM YIELD =     .100000E-02 MOLES CONVERTED PER
          PHOTON ABSORBED) .001

ENTER MULTIPLICATIVE FACTOR TO ALLOW FOR NATURALLY OCCURRING LIGHT
         ABSORBERS, QUENCHERS, AND SENSITIZERS (CURRENT AQS MULTIPLICATIVE
         FACTOR =     1.000)  1.0
```



```
TOTAL PHOTONS ABSORBED (IN PHOTONS / (MOLE * CM**3 * S) FOR
    EACH COMPARTMENT ARE
                   LEAVES         GRASS          LITTER        SOIL
  CANOPY         .1860E+18      .6220E+17      .1040E+18      0.
  ALLEY          0.             .1040E+18      .1450E+18      0.

DO YOU WISH TO CHANGE ANY ENTRIES? (1) YES  (2) NO 2

MULTIPLICATIVE FACTOR FOR HYDROLYSIS DUE TO AIR TEMP.
IS OF THE FORM

          F = E ** (DELHA/1.986) * (T - TO) / (T * TO) )

          WHERE E = NATURAL LOG BASE = 2.718
                T = AIR TEMPERATURE (DEGREES K)
                TO = 296 DEGREES K
                DELHA = ACTIVATION ENERGY (CALORIES/MOLE)

ENTER ACTIVATION ENERGY FOR ABOVE EQUATION
        (CURRENT ACTIVATION ENERGY = 12500.00 CAL/MOLE) 12500.

MULTIPLICATIVE FACTOR FOR HYDROLYSIS DUE TO SOIL TEMP.
IS OF THE FORM

          F = E ** (SDELHA/1.986) * (T - TO) / (T * TO) )

          WHERE E = NATURAL LOG BASE = 2.718
                T = SOIL TEMPERATURE (DEGREES K)
                TO = 296 DEGREES K
                SDELHA = ACTIVATION ENERGY (CALORIES/MOLE)

ENTER ACTIVATION ENERGY FOR ABOVE EQUATION
        (CURRENT ACTIVATION ENERGY = 13500.00 CAL/MOLE)12500.
```

The user is next asked if he wishes to change coefficients of attenuation equations based on environmental conditions. If he selects this option, he is required to select a specific attenuation process (microbial degradation, photolysis, hydrolysis, volatilization, oxidation). The appropriate equations are displayed one at a time and the user may enter new coefficients if desired.

Example

```
DO YOU WISH TO CHANGE COEFFICIENTS OF ATTENUATION EQUATIONS
DEPENDENT ON ENVIRONMENTAL CONDITIONS
          (1) YES  (2) NO 1

DO YOU WISH TO CHANGE COEFFICIENTS OF EQUATIONS  DEPENDENT ON ENVIRONMENTAL
CONDITIONS FOR
          (1) MICROBIAL DEGRADATION  (2) HYDROLYSIS  (3) OXIDATION 1

MULTIPLICATIVE FACTOR FOR MICROBIAL DEGRADATION BASED ON PERCENT ORGANIC MATTER
IS OF THE FORM

          F = (1.0 + E**(A * (PERCENT ORGANIC MATTER - B)))**C

           WHERE A =    .079
                 B =  -1.850
                 C =   1.870
                 E = NATURAL LOG BASE = 2.718

DO YOU WISH TO CHANGE THESE COEFFICIENTS?   (1) YES   (2) NO 2

MULTIPLICATIVE FACTOR FOR MICROBIAL DEGRADATION BASED ON SOIL TEMPERATURE
IS OF THE FORM

          F = A + B * SOILTEMP + C * (SOILTEMP**2)
            FOR 5 (DEG. C) < SOILTEMP < 52 (DEG. C
     AND F = 0.0   OTHERWISE

           WHERE A = -.19520
                 B =  .04480
                 C =  .00080

DO YOU WISH TO CHANGE THESE COEFFICIENTS?   (1) YES   (2) NO 2

DO YOU TO CHANGE OTHER COEFFICIENTS TO  ATTENUATION EQUATIONS?
          (1) YES  (2) NO 1

DO YOU WISH TO CHANGE COEFFICIENTS OF EQUATIONS  DEPENDENT ON ENVIRONMENTAL
CONDITIONS FOR
          (1) MICROBIAL DEGRADATION  (2) HYDROLYSIS  (3) OXIDATION 2

MULTIPLICATIVE FACTOR FOR HYDROLYSIS BASED ON PH VALUE           -
IS OF THE FORM

          F = 1.0          ,IF PH   C
          F = A * PH + B   ,IF PH =  C

           WHERE A =  10.490
                 B = -76.810
                 C =   7.430
```

```
ANY MORE REPARAMETERIZATION? (1) YES  (2) NO 1

DO YOU WISH TO CHANGE (1) PHYSICAL CHARACTERISTICS OF SITE
         (2) ATTENUATION PARAMETERS (3) PENETRATION PARAMETERS
         (4) MOVEMENT PARAMETERS (5) ORGANISM PARAMETERS 3

CURRENT INITIAL PENETRATION PROPORTIONS ARE:

             LEAVES     GRASS     LITTER
                .081       .240       .255

WOULD YOU LIKE TO CHANGE THE INITIAL PENETRATION PROPORTIONS OF A SPRAY
         (1) YES  (2) NO 2

CURRENT DAILY PENETRATION PROPORTIONS ARE:

             LEAVES     GRASS     LITTER
  CANOPY       0.000     0.000       .126
  ALLEY        0.000     0.000       .156

WOULD YOU LIKE TO CHANGE DAILY PENETRATION PROPORTIONS?  (1) YES  (2) NO 2

CURRENT DAILY PENETRATED RESIDUE ATTENUATION PROPORTIONS ARE:

             LEAVES     GRASS     LITTER
  CANOPY        .010      .010       .010
  ALLEY         .010      .010       .010

WOULD YOU LIKE TO CHANGE DAILY PENETRATION ATTENUATION PROPORTIONS
         (1) YES  (2) NO 2
```

3. Penetration Parameters

There are three basic penetration parameters for each region and layer in a matrix form. They represent 1) the initial penetration rate for a spray, 2) the daily penetration proportion of dislodgeable residue that becomes penetrated, and 3) the penetrated residue attenuation proportions.

First, the initial (day of spray) penetration matrix is printed. The user may change any of the entries one at a time. When this is completed, the new matrix is printed out. Second, the daily penetration rate matrix is printed. The user may again change any of the entries one at a time. When completed, the new matrix will be printed. Finally the penetrated residue attenuation matrix is allowed to be altered in the same manner.

Example

```
DO YOU WISH TO CHANGE THESE COEFFICIENTS?   (1) YES   (2) NO 2

DO YOU TO CHANGE OTHER COEFFICIENTS TO  ATTENUATION EQUATIONS?
         (1) YES  (2) NO1

DO YOU WISH TO CHANGE COEFFICIENTS OF EQUATIONS  DEPENDENT ON ENVIRONMENTAL
CONDITIONS FOR
         (1) MICROBIAL DEGRADATION  (2) HYDROLYSIS  (3) OXIDATION 3

MULTIPLICATIVE FACTOR FOR OXIDATION IS OF THE FORM:
        F = A

          WHERE A = 1.000

DO YOU WISH TO CHANGE THESE COEFFICIENTS?   (1) YES   (2) NO 2

DO YOU TO CHANGE OTHER COEFFICIENTS TO  ATTENUATION EQUATIONS?
         (1) YES  (2) NO 2
```

4. Movement Parameters

A. SPRAY DISTRIBUTION

The first movement parameter the user is allowed to change is the spray distribution. The spray distribution represents the proportion of pesticide reaching the orchard during spraying that goes to each distinct (region and layer) compartment. The current spray distribution vector is displayed. The user may use this or enter a new spray distribution vector. If he enters a new spray distribution vector, he must enter a proportion for each layer and region. The sum of the proportions he enters must be 1.0. If it is not, it is normalized to one. (Note--drift losses are accounted for elsewhere in the model.) When completed, the new spray distribution vector is printed.

Example

```
ANY MORE REPARAMETERIZATION? (1) YES  (2) NO 1

DO YOU WISH TO CHANGE (1) PHYSICAL CHARACTERISTICS OF SITE
        (2) ATTENUATION PARAMETERS (3) PENETRATION PARAMETERS
        (4) MOVEMENT PARAMETERS (5) ORGANISM PARAMETERS 4

CURRENT SPRAY DISTRIBUTION IS:

              LEAVES      GRASS     LITTER      SOIL
  CANOPY        .5392      .1006      .0387      .0299
  ALLEY        0.0000      .0942      .0300      .1564

DO YOU WANT TO ENTER A NEW SPRAY DISTRIBUTION? (1) YES  (2) NO 2
```

B. NON-RAIN MOVEMENT MATRIX

After the spray distribution matrix is complete, the non-rain movement matrix is printed. The non-rain movement matrix represents the daily proportions of pesticides that move from one compartment to another (see Subroutine Non-Rain description for more details about how the matrix is applied).

The user has the option to 1) re-enter any single column of the matrix, 2) display the matrix after changes have been made, 3) increase or decrease the daily proportion of movement of the entire matrix by any multiplicative factor, 4) increase or decrease the daily proportion of a single column by any multiplicative factor, or 5) exit the non-rain movement matrix change mode. He may make any number of changes (1) through (4) until he exits the change mode. Note--options (3) and (4) do not act directly on the matrix entries. They cause the factor entered to be multiplied by the appropriate instantaneous rates calculated from the off-diagonal elements. The (multiplied) rates are then reconverted to 1-day loss proportions, and the diagonal elements recomputed by subtraction. Thus a factor of 2 has the effect of making the pesticide "half as sticky", while .5 makes it "twice as sticky".

Example

```
CURRENT NON-RAIN MOVEMENT MATRIX

                                                FROM
                C 1      C 2      C 3      C 4      A 1      A 2      A 3      A 4

          C1   0.9804
          C2   0.0003   0.9347
          C3   0.0088   0.0654   0.9073
          C4   0.0000   0.0000   0.0927   1.0000
   TO     A1
          A2   0.0001                                       0.9732
          A3   0.0094                                       0.0265   0.9962
          A4   0.0005                                       0.0003   0.0038   1.0000

WHERE C=CANOPY REGION, A=ALLEY REGION
      1=LEAVES, 2=GRASS, 3=LITTER-MOSS, 4=SOIL
      AND COLUMNS MUST SUM TO 1.0
```

```
DO YOU WISH (1) TO RE-ENTER A SINGLE COLUMN
         (2) LOOK AT THE CURRENT NON-RAIN MOVEMENT MATRIX
         (3) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE MOVEMENT
         MATRIX BY A MULTIPLICATIVE FACTOR
         (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
         MULTIPLICATIVE FACTOR
         (5) EXIT NON-RAIN MATRIX CHANGE MODE 4

ENTER REGION (1) CANOPY  (2) ALLEY
      LAYER (1) LEAVES  (2) GRASS  (3) LITTERMOSS  (4) SOIL
      OF THE COLUMN VECTOR YOU WISH TO CHANGE 1 1

ENTER FACTOR YOU WISH TO INCREASE OR DECREASE THE RATE OF MOVEMENT BY
         (FACTOR MUST BE GREATER THAN ZERO) 2.0

DO YOU WISH (1) TO RE-ENTER A SINGLE COLUMN
         (2) LOOK AT THE CURRENT NON-RAIN MOVEMENT MATRIX
         (3) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE MOVEMENT
         MATRIX BY A MULTIPLICATIVE FACTOR
         (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
         MULTIPLICATIVE FACTOR
         (5) EXIT NON-RAIN MATRIX CHANGE MODE2

CURRENT NON-RAIN MOVEMENT MATRIX

                                         FROM
                  C 1    C 2    C 3    C 4    A 1    A 2    A 3    A 4
          C 1    .9611
          C 2    .0006  .9347
          C 3    .0175  .0654  .9073
          C 4   0.0000 0.0000  .0927 1.0000
   TO     A 1
          A 2    .0002                              .9732
          A 3    .0186                              .0265  .9962
          A 4    .0011                              .0003  .0038 1.0000

WHERE C=CANOPY REGION, A=ALLEY REGION
      1=LEAVES, 2=GRASS, 3=LITTERMOSS, 4=SOIL
      AND COLUMNS MUST SUM TO 1.0

DO YOU WISH (1) TO RE-ENTER A SINGLE COLUMN
         (2) LOOK AT THE CURRENT NON-RAIN MOVEMENT MATRIX
         (3) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE MOVEMENT
         MATRIX BY A MULTIPLICATIVE FACTOR
         (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
         MULTIPLICATIVE FACTOR
         (5) EXIT NON-RAIN MATRIX CHANGE MODE 5
```

C. RAINFALL MOVEMENT MATRICES

(See SUBROUTINE RAINFALL for description of how matrix is applied.)

The user is first asked which matrix to display (light or heavy rainfall). The changes made to a rainfall matrix are always to the last rainfall matrix (light or heavy) that was displayed.

When asked to make changes, the user may always display either the light or heavy rainfall movement matrix.

Other than this, changes to rainfall movement matrices are the exact same options as those to the non-rain movement matrix. In the heavy rainfall matrix example below, the movement rate is first doubled, then cut in half to restore the matrix to its original values.

Example

```
DO YOU WISH TO (1) LOOK AT LIGHT RAINFALL MOVEMENT MATRIX
          (2) LOOK AT HEAVY RAINFALL MOVEMENT MATRIX
          (3) MAKE NO RAINFALL MOVEMENT MATRIX CHANGES 1

CURRENT LIGHT RAINFALL MOVEMENT MATRIX

                                            FROM
                   C 1     C 2    C 3    C 4    A 1     A 2    A 3    A 4
          C 1     .9320
          C 2     .0296   .7468
          C 3     .0021   .0708 1.0000
          C 4     .0362   .1824 0.0000 1.0000
   TO     A 1
          A 2     .0001                                 .8687
          A 3    0.0000                                0.0000 1.0000
          A 4    0.0000                                 .1313 0.0000 1.0000

WHERE C=CANOPY REGION, A=ALLEY REGION
      1=LEAVES, 2=GRASS, 3=LITTERMOSS, 4=SOIL
      AND COLUMNS MUST SUM TO 1.0

DO YOU WISH TO (1) LOOK AT CURRENT LIGHT RAINFALL MATRIX
          (2) LOOK AT CURRENT HEAVY RAINFALL MATRIX
          (3) RE-ENTER A SINGLE COLUMN OF THE RAINFALL MATRIX YOUR WORKING ON
          (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE CURRENT
          MOVEMENT MATRIX BY ANY MULTIPLICATIVE FACTOR
          (5) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
          MULTIPLICATIVE FACTOR
          (6) EXIT RAINFALL MATRIX CHANGE MODE 4
```

```
ENTER FACTOR YOU WISH TO INCREASE OR DECREASE THE RATE OF MOVEMENT BY
         (FACTOR MUST BE GREATER THAN ZERO) 2.

DO YOU WISH TO (1) LOOK AT CURRENT LIGHT RAINFALL MATRIX
         (2) LOOK AT CURRENT HEAVY RAINFALL MATRIX
         (3) RE-ENTER A SINGLE COLUMN OF THE RAINFALL MATRIX YOUR WORKING ON
         (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE CURRENT
         MOVEMENT MATRIX BY ANY MULTIPLICATIVE FACTOR
         (5) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
         MULTIPLICATIVE FACTOR
         (6) EXIT RAINFALL MATRIX CHANGE MODE 1

CURRENT LIGHT RAINFALL MOVEMENT MATRIX

                                         FROM
                  C 1    C 2    C 3    C 4    A 1    A 2    A 3    A 4
          C 1    .8686
          C 2    .0572  .5577
          C 3    .0041  .1237 1.0000
          C 4    .0699  .3186 0.0000 1.0000
   TO     A 1
          A 2    .0002                              .7546
          A 3   0.0000                             0.0000 1.0000
          A 4   0.0000                              .2454 0.0000 1.0000

WHERE C=CANOPY REGION, A=ALLEY REGION
      1=LEAVES, 2=GRASS, 3=LITTERMOSS, 4=SOIL
      AND COLUMNS MUST SUM TO 1.0

DO YOU WISH TO (1) LOOK AT CURRENT LIGHT RAINFALL MATRIX
         (2) LOOK AT CURRENT HEAVY RAINFALL MATRIX
         (3) RE-ENTER A SINGLE COLUMN OF THE RAINFALL MATRIX YOUR WORKING ON
         (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE CURRENT
         MOVEMENT MATRIX BY ANY MULTIPLICATIVE FACTOR
         (5) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
         MULTIPLICATIVE FACTOR
         (6) EXIT RAINFALL MATRIX CHANGE MODE 4

ENTER FACTOR YOU WISH TO INCREASE OR DECREASE THE RATE OF MOVEMENT BY
         (FACTOR MUST BE GREATER THAN ZERO) 0.5

DO YOU WISH TO (1) LOOK AT CURRENT LIGHT RAINFALL MATRIX
         (2) LOOK AT CURRENT HEAVY RAINFALL MATRIX
         (3) RE-ENTER A SINGLE COLUMN OF THE RAINFALL MATRIX YOUR WORKING ON
         (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE CURRENT
         MOVEMENT MATRIX BY ANY MULTIPLICATIVE FACTOR
         (5) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
         MULTIPLICATIVE FACTOR
         (6) EXIT RAINFALL MATRIX CHANGE MODE 1
```

```
CURRENT LIGHT RAINFALL MOVEMENT MATRIX

                                               FROM
                       C 1    C 2    C 3    C 4    A 1    A 2    A 3    A 4
              C 1      .9320
              C 2      .0296  .7468
              C 3      .0021  .0708 1.0000
              C 4      .0362  .1824 0.0000 1.0000
       TO     A 1
              A 2      .0001                              .8687
              A 3     0.0000                             0.0000 1.0000
              A 4     0.0000                              .1313 0.0000 1.0000

WHERE C=CANOPY REGION, A=ALLEY REGION
      1=LEAVES, 2=GRASS, 3=LITTERMOSS, 4=SOIL
      AND COLUMNS MUST SUM TO 1.0

DO YOU WISH TO (1) LOOK AT CURRENT LIGHT RAINFALL MATRIX
          (2) LOOK AT CURRENT HEAVY RAINFALL MATRIX
          (3) RE-ENTER A SINGLE COLUMN OF THE RAINFALL MATRIX YOUR WORKING ON
          (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE CURRENT
          MOVEMENT MATRIX BY ANY MULTIPLICATIVE FACTOR
          (5) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
          MULTIPLICATIVE FACTOR
          (6) EXIT RAINFALL MATRIX CHANGE MODE 2

CURRENT HEAVY RAINFALL MOVEMENT MATRIX

                                               FROM
                       C 1    C 2    C 3    C 4    A 1    A 2    A 3    A 4
              C 1      .8209
              C 2      .0202  .6126
              C 3      .0957 0.0000 1.0000
              C 4      .0082  .3874 0.0000 1.0000
       TO     A 1
              A 2      .0270                              .2798
              A 3      .0008                              .4465 1.0000
              A 4      .0272                              .2737 0.0000 1.0000

WHERE C=CANOPY REGION, A=ALLEY REGION
      1=LEAVES, 2=GRASS, 3=LITTERMOSS, 4=SOIL
      AND COLUMNS MUST SUM TO 1.0

DO YOU WISH TO (1) LOOK AT CURRENT LIGHT RAINFALL MATRIX
          (2) LOOK AT CURRENT HEAVY RAINFALL MATRIX
          (3) RE-ENTER A SINGLE COLUMN OF THE RAINFALL MATRIX YOUR WORKING ON
          (4) CHANGE THE DAILY PROPORTION OF MOVEMENT OF THE ENTIRE CURRENT
          MOVEMENT MATRIX BY ANY MULTIPLICATIVE FACTOR
          (5) CHANGE THE DAILY PROPORTION OF MOVEMENT OF A SINGLE COLUMN BY A
          MULTIPLICATIVE FACTOR
          (6) EXIT RAINFALL MATRIX CHANGE MODE 6
```

D. PROPORTION OF GRASS MOWED

Finally the user is shown the current proportion of grass mowed for a mow date, and asked if he would like to enter a new one. If so, the porportion must be ≥ 0.0 and ≤ 1.0.

<u>Example</u>

```
WOULD YOU LIKE TO CHANGE THE PROPORTION OF GRASS MOWED
(CURRENT PROPORTION MOWED =0.0000)  (1) YES  (2) NO 1

ENTER PROPORTION OF GRASS MOWED ( 0.0 TO 1.0) 0.40
```

Example Run of POEM

In the following sample run, the user opted to use weather data supplied on a file, but to enter spray dates manually. The user specified printout of pesticide residues at 5 day intervals, running of only the isopod (Tracheoniscus) model, and other choices as shown. Files for plotting pesticide residues and isopod populations were also created by the run.

Example

```
 EXEC BEGUN.16.18.58.

THE FOLLOWING OPTIONS ARE ON BY DEFAULT

           ORGANISM SUBMODEL
           ATTENUATION SUBMODEL
           NON-RAIN MOVEMENT SUBMODEL
           PESTICIDE APPLICATION SUBMODEL
           RAINFALL MOVEMENT SUBMODEL
           PENETRATION SUBMODEL
           WRITE FILES FOR PLOTTING PACKAGE
           VARIABLE   ATTENUATION

OTHER AVAILABLE OPTIONS ARE

           MOWER SUBMODEL
           WEATHER SIMULATOR
           SOIL MOISTURE SIMULATOR
           LEAF GROWTH SUBMODEL
           MOVEMENT MATRIX DAILY OUTPUT
           SOIL TRANSPORTATION SUBMODEL
           PESTICIDE PRINTOUT
           NON-DEFAULT EVENT DATES -SPRAYS,MOWS,ETC

DO YOU WISH TO TURN ON OR OFF ANY OPTIONS?
        (1) YES  (2) NO 1
```

```
ENTER A VALUE FOR EACH OPTION
         (1) FOR OPTION ON  (2) FOR OPTION OFF
    OPTION  1     ORGANISM SUBMODEL 1
    OPTION  2     MOWER SUBMODEL 2
    OPTION  3     ATTENUATION SUBMODEL 1
    OPTION  4     WEATHER SIMULATOR 2
    OPTION  5     NON-RAIN MOVEMENT SUBMODEL 1
    OPTION  6     PESTICIDE APPLICATION SUBMODEL 1
    OPTION  7     RAINFALL MOVEMENT SUBMODEL 1
    OPTION  8     PENETRATION SUBMODEL  1
    OPTION  9     SOIL MOISTURE SIMULATOR 2
    OPTION 10     LEAF GROWTH SUBMODEL 2
    OPTION 11     MOVEMENT MATRIX DAILY OUTPUT 2
    OPTION 12     SOIL TRANSPORTATION SUBMODEL 2
    OPTION 13     PESTICIDE PRINTOUT 1
    OPTION 14     WRITE FILES FOR PLOTTING PACKAGE 1
    OPTION 15     NON-DEFAULT EVENT DATES -SPRAYS,MOWS,ETC 1
    OPTION 16     VARIABLE   ATTENUATION 1

WHICH ORGANISM SUBMODELS ARE DESIRED (1) YES (2) NO
TRACHEONISCUS? 1
FOLSOMIA? 2
SPIDER? 2
EARTHWORM? 2

HOW MANY YEARS DO YOU WISH TO SIMULATE( ONE TO TEN YEARS) 1

HOW OFTEN (IN DAYS) WOULD YOU LIKE PESTICIDE VALUES PRINTED TO OUTPUT 5

DO YOU WANT TO REPARAMETERIZE THE MODEL (DEFAULT VALUES ARE BASED
    ON ESTIMATES FOR AZINPHOSMETHYL AS GUTHION 50 W.P.)
         (1) YES   (2) NO 2


*******************************************************************************
                                   YEAR  1
*******************************************************************************



ENTER SEASON STARTING DATE 170

ENTER SEASON ENDING DATE 230

HOW MANY SPRAYS DO YOU WISH THIS SEASON( ZERO TO TEN SPRAYS) 2

ENTER DATES CHRONOLOGICALLY

SPRAY DATE  1? 170
DOSAGE( IN KG./HA.) FOR SPRAY  1? 2.0
SPRAY DATE  2? 184
DOSAGE( IN KG./HA.) FOR SPRAY  2? 2.0

SPRAY DATE, DAY  170, SPRAY RATE =  2.00 KG/HA, PERCENT DRIFT OF SPRAY =  50.8
```

```
PREDICTED PESTICIDE LEVELS FOR DAY  170
                 DISLODGEABLE RESIDUES                                PENETRATED RESIDUES
              LEAVES  GRASS LITTERMOSS SOIL                       LEAVES  GRASS LITTERMOSS SOIL
CANOPY        6.559   1.012     .382   0.000                        .578    .320     .130    .396
ALLEY                  .561     .175   0.000                                .177     .060   1.226


PREDICTED PESTICIDE LEVELS FOR DAY  175
                 DISLODGEABLE RESIDUES                                PENETRATED RESIDUES
              LEAVES  GRASS LITTERMOSS SOIL                       LEAVES  GRASS LITTERMOSS SOIL
CANOPY        4.697    .601     .384   0.000                        .550    .304     .372    .354
ALLEY                  .356     .175   0.000                                .169     .196    .717


PREDICTED PESTICIDE LEVELS FOR DAY  180
                 DISLODGEABLE RESIDUES                                PENETRATED RESIDUES
              LEAVES  GRASS LITTERMOSS SOIL                       LEAVES  GRASS LITTERMOSS SOIL
CANOPY        3.324    .353     .279   0.000                        .523    .289     .565    .314
ALLEY                  .221     .132   0.000                                .160     .307    .429

RAIN DATE, HEAVY RAIN DAY  182

SPRAY DATE, DAY  184, SPRAY RATE =  2.00 KG/HA, PERCENT DRIFT OF SPRAY =  39.0


PREDICTED PESTICIDE LEVELS FOR DAY  184
                 DISLODGEABLE RESIDUES                                PENETRATED RESIDUES
              LEAVES  GRASS LITTERMOSS SOIL                       LEAVES  GRASS LITTERMOSS SOIL
CANOPY       10.220   1.445     .826   0.000                       1.219    .674     .889    .912
ALLEY                  .777     .363   0.000                                .374     .466   1.890


PREDICTED PESTICIDE LEVELS FOR DAY  185
                 DISLODGEABLE RESIDUES                                PENETRATED RESIDUES
              LEAVES  GRASS LITTERMOSS SOIL                       LEAVES  GRASS LITTERMOSS SOIL
CANOPY        9.563   1.303     .798   0.000                       1.206    .667     .983    .888
ALLEY                  .710     .353   0.000                                .370     .518   1.712


PREDICTED PESTICIDE LEVELS FOR DAY  190
                 DISLODGEABLE RESIDUES                                PENETRATED RESIDUES
              LEAVES  GRASS LITTERMOSS SOIL                       LEAVES  GRASS LITTERMOSS SOIL
CANOPY        6.765    .765     .582   0.000                       1.147    .634    1.374    .719
ALLEY                  .441     .267   0.000                                .352     .736    .983
```

```
PREDICTED PESTICIDE LEVELS FOR DAY  195
            DISLODGEABLE RESIDUES                     PENETRATED RESIDUES
          LEAVES  GRASS LITTERMOSS SOIL            LEAVES  GRASS LITTERMOSS SOIL
CANOPY    4.765    .449     .390   0.000           1.091    .603   1.613    .541
ALLEY              .272     .187   0.000                    .334    .876    .547


PREDICTED PESTICIDE LEVELS FOR DAY  200
            DISLODGEABLE RESIDUES                     PENETRATED RESIDUES
          LEAVES  GRASS LITTERMOSS SOIL            LEAVES  GRASS LITTERMOSS SOIL
CANOPY    3.369    .265     .258   0.000           1.038    .574   1.738    .388
ALLEY              .169     .130   0.000                    .318    .956    .300

RAIN DATE, HEAVY RAIN DAY  203


PREDICTED PESTICIDE LEVELS FOR DAY  205
            DISLODGEABLE RESIDUES                     PENETRATED RESIDUES
          LEAVES  GRASS LITTERMOSS SOIL            LEAVES  GRASS LITTERMOSS SOIL
CANOPY    1.938    .140     .304   0.000            .987    .545   1.844    .381
ALLEY              .065     .115   0.000                    .302   1.010    .227

RAIN DATE, LIGHT RAIN DAY  208

RAIN DATE, HEAVY RAIN DAY  210


PREDICTED PESTICIDE LEVELS FOR DAY  210
            DISLODGEABLE RESIDUES                     PENETRATED RESIDUES
          LEAVES  GRASS LITTERMOSS SOIL            LEAVES  GRASS LITTERMOSS SOIL
CANOPY    1.042    .086     .259   0.000            .938    .519   1.890    .370
ALLEY              .030     .074   0.000                    .288   1.027    .157

RAIN DATE, LIGHT RAIN DAY  214


PREDICTED PESTICIDE LEVELS FOR DAY  215
            DISLODGEABLE RESIDUES                     PENETRATED RESIDUES
          LEAVES  GRASS LITTERMOSS SOIL            LEAVES  GRASS LITTERMOSS SOIL
CANOPY     .694    .060     .101   0.000            .892    .493   1.907    .294
ALLEY              .017     .036   0.000                    .274   1.018    .091

RAIN DATE, HEAVY RAIN DAY  218
```

```
PREDICTED PESTICIDE LEVELS FOR DAY  220
             DISLODGEABLE RESIDUES                          PENETRATED RESIDUES
           LEAVES  GRASS LITTERMOSS SOIL                 LEAVES  GRASS LITTERMOSS SOIL
CANOPY      .408    .031     .077   0.000                 .849    .469   1.872     .220
ALLEY               .011     .023   0.000                         .260    .992     .065


PREDICTED PESTICIDE LEVELS FOR DAY  225
             DISLODGEABLE RESIDUES                          PENETRATED RESIDUES
           LEAVES  GRASS LITTERMOSS SOIL                 LEAVES  GRASS LITTERMOSS SOIL
CANOPY      .289    .019     .031   0.000                 .807    .446   1.813     .14[illegible]
ALLEY               .007     .012   0.000                         .247    .957     .038

RAIN DATE, HEAVY RAIN DAY  228


PREDICTED PESTICIDE LEVELS FOR DAY  230
             DISLODGEABLE RESIDUES                          PENETRATED RESIDUES
           LEAVES  GRASS LITTERMOSS SOIL                 LEAVES  GRASS LITTERMOSS SOIL
CANOPY      .170    .011     .029   0.000                 .767    .424   1.744     .100
ALLEY               .004     .009   0.000                         .235    .918     .027
      END  ORCHARD
     077000   FINAL EXECUTION FL.
      5.068 CP SECONDS EXECUTION TIME.
```

Producing Graphs

The two plotting programs described below have been written to allow the researchers to conveniently generate Tektronix (CRT) or CALCOMP (pen-and-ink) graphs of pesticide and population levels as generated by POEM. Because they must utilize locally-determined procedures for plotting, they depend on MSU-provided software which is not generally available. Thus, for other sites, more general-purpose plotting packages should be used, working from POEM-generated files as input. These descriptions are provided to illustrate an example working environment in which POEM is conveniently utilized.

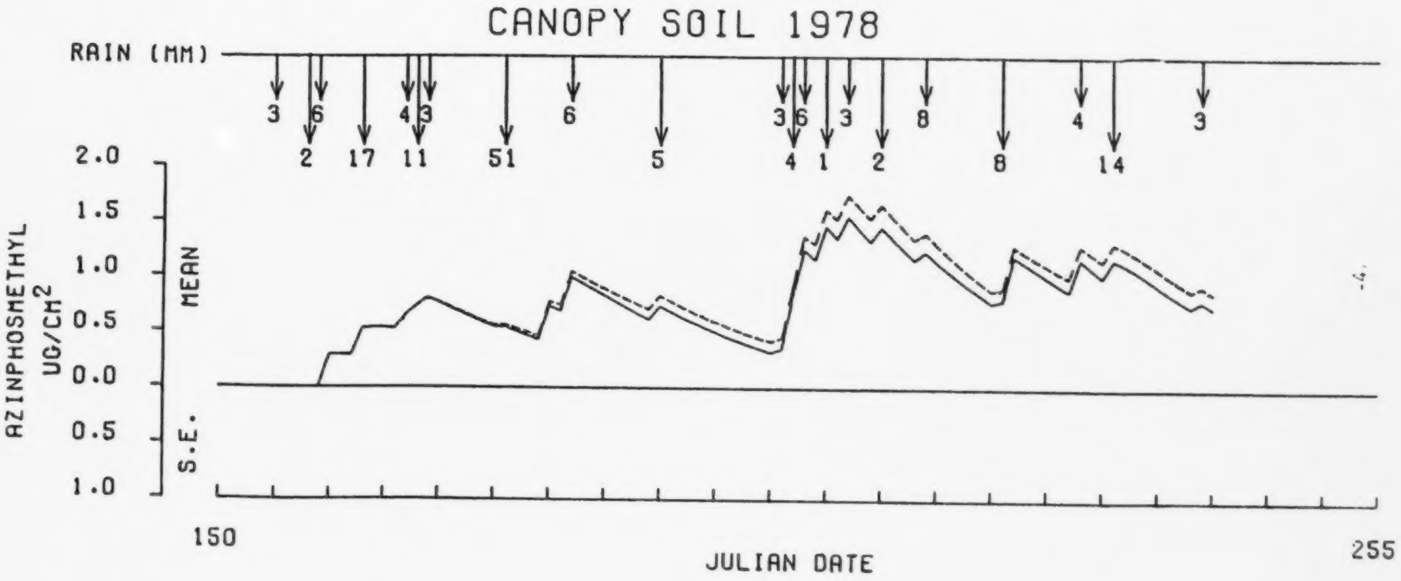
Pesticide Graphs

Program ORCHARDCALPLOT allows the user to plot pesticide levels in any region or layer versus time, producing either CALCOMP or TEKTRONIX output. It has available multiple output formats, depending on the user's needs. It can plot the level in a single region based on a single POEM run, or can plot one solid and one dashed line, based on two runs, for A, B comparison purposes. It can also display with vertical bars a set of data (usually measured levels, at irregular intervals) for comparison with predicted levels.

The program begins by asking whether TEKTRONIX or CALCOMP plotting is desired. It then presents the user a set of options:

Example

```
ENTER 1 FOR TEK, 2 FOR CALCOMP...1

PLOTTING OPTIONS---
         (1) MEASURED AVERAGES ONLY
         (2) MEASURED AVERAGES WITH ONE PREDICTED SET
         (3) MEASURED AVERAGES WITH TWO PREDICTED SETS
         (4) ONE PREDICTED SET ONLY (NO MEASURED AVERAGES)
         (5) TWO PREDICTED SETS WITH NO MEASURED AVERAGESS

WHAT IS THE BEGINNING YEAR( 1 TO 4)?1

WHAT IS THE ENDING YEAR(1 TO 4, AND >= TO BEGINNING YEAR)?1
```


CANOPY SOIL 1978
RAIN (MM)
3
2
6
17
4
11
3
51
6
5
3
4
6
1
3
2
8
8
4
14
3
AZINPHOSMETHYL UG/CM^2
2.0
1.5
1.0
0.5
0.0
0.5
1.0
MEAN
S.E.
150
255
JULIAN DATE

The user needs to make sure that appropriate files are available for the option he selects. A single file of predicted residues to be graphed in a solid line must be called TAPE1. An (optional) second file to appear as a dashed line must be called TAPE4. If measured values are to be plotted, they must be called TAPE5. (For plots of outputs of single POEM runs, the correct file is automatically available as TAPE1.) In addition, two files which specify the dates of pesticide spraying and the dates and amounts of rain must be available as TAPE2 and TAPE3, respectively. If a POEM run has just been made, the appropriate TAPE2 and TAPE3 have been created by POEM.

For information on file handling on the MSU Cyber system, see the section on Attaching Tapes.

Organism Graphs

Program ORGPLOT allows the user to plot population levels versus time for single life-stages or groups of life-stages. It uses the files generated by POEM (called TAPE11, TAPE12, TAPE13, TAPE14, TAPE15). They are created by POEM as follows:

TAPE11--non-breeding female isopod populations on each day of the model run, arranged as:

	IN ORGPLOT, LIFESTAGE INDEX
Day Number (Jan. 1 year 1 = day 1)	-----
daily egg hatch (not number of eggs present)	1
size-class 1 (0.5-1.34 mg)	2
size-class 2 (1.35-5.0 mg)	3
size-class 3 (5.01-12.0 mg)	4
size-class 4 (12.01-30.0 mg)	5
size-class 5 (30.01-50.0 mg)	6
size-class 6 (50.01-80.0 mg)	7
size-class 7 (>80.0 mg)	8
total, classes 1-7 (lifestage indices 2-8)	9

TAPE12--breeding female isopod populations on each day of the model run, arranged as:

Day Number	
Blank field (egg hatch stored on TAPE11)	
size-class 1-3 0.0 (no small breeders)	
size-class 4 (12.01-30.0 mg)	5
size-class 5 (30.01-50.0 mg)	6

	IN ORGPLOT, LIFESTAGE INDEX
size-class 6 (50.01-80.0 mg)	7
size-class 7 (>80.0 mg)	8
total, classes 4-7 (life-stage indices 5-8)	9

(Note that in ORGPLOT, the populations displayed are the sums of breeding and non-breeding populations.)

TAPE13--collembola (also called Folsomia in the model, based on data from both *Folsomia candida* and *Folsomia quadrioculata*) populations on each day of the model run, arranged as:

Day Number	
Egg *hatch* on current day (*not* total eggs present)	1
Prejuveniles	2
Juveniles	3
Adults	4
Totals (lifestage indices 2-4)	5

TAPE14--earthworm populations (see earthworm model for definitions)

TAPE15--spider populations on each day of the model run, arranged as:

Day Number	
viable eggs (*not* hatch)	1
Instar 1	2
⋮	⋮
Instar 8	9
Adults	10
Totals (including eggs)	11

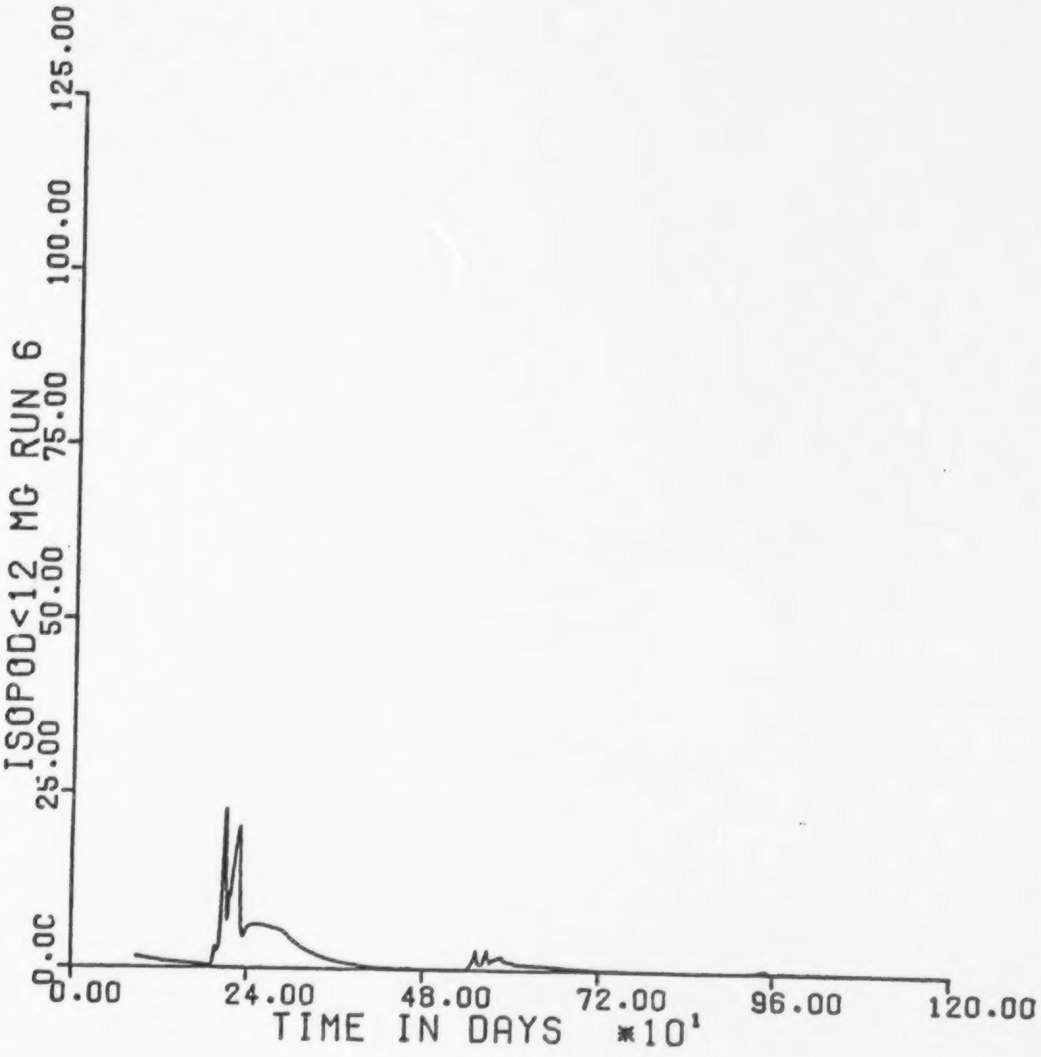
ORGPLOT will expect to find only those files which the user asks to plot (i.e., for isopods--TAPE11, TAPE12, for collembola--TAPE13, for earthworms--TAPE14, for spiders--TAPE15). The user is asked for the choice of organisms, a label for the y-axis, and for scale factors for each axis. The x-axis will be scaled at 6 points (with 5 intervals between), and the user may explicitly enter the starting and ending Julian dates (cumulative--i.e., 370 is day 5 of year 2), or may enter 0,0 to request auto-scaling by the program. A maximum of 1200 days may be displayed. Similarly, the y-(population) axis can be scaled by specifying an upper limit, or the program will auto-scale it if a 0 is entered.

The user is next asked for a size-class range to plot. This is given by specifying the number of the beginning and ending size-classes, in ascending order--i.e., for size classes 2-4, enter 2,4; to see only size-class 3, enter 3,3.

After a graph is generated, the user may shoot a hard copy (TEKTRONIX) before the program contaminates the screen with any further questions. When ready to proceed, the user should type a space and return, to produce the next question. He may request another graph, or may quit the program. In CALCOMP mode, the program immediately prompts for further actions, after indicating that the plot file has been submitted for plotting (an off-line procedure).

Example

```
ENTER 1 FOR TEK, 2 FOR CALCOMP: 1

WHICH ORGANISM DO YOU WISH TO PLOT
          (1) TRACHEONISCUS
          (2) FOLSOMIA
          (3) SPIDER
          (4) EARTHWORM 1

ENTER Y-AXIS LABEL FOR GRAPH SAMPLE ISOPODS

ENTER X LOWER, UPPER LIMITS, OR 0,0 FOR AUTOMATIC: 0,0

ENTER Y UPPER LIMIT, OR 0 FOR AUTOMATIC: 0

ENTER LIFESTAGE RANGE TO PLOT; LOWER,UPPER INDICES: 2,4
```


ISOPOD<12 MG RUN 6
0.0C
25.00
50.00
75.00
100.00
125.00
0.00
24.00
48.00
72.00
96.00
120.00
TIME IN DAYS *10¹

Attaching Tapes

Disk files which are to be read or written during the operation of POEM and its associated plotting programs on MSU's CYBER are locally referred to as TAPEs. This naming is to agree with local file names specified in the PROGRAM statement at the beginning of each program. At MSU, there are two types of disk files: local files and permanent files. Permanent files may be read and/or written only by "attaching" them to (temporary) local file names. TAPE1, TAPE2, etc., are examples of such local file names. Thus, if the user wants to plot data from permanent files stored after earlier runs (see below), he must first "attach" the permanent files to local files, as shown below:

```
ATTACH,TAPE1,PREDICTEDRUN1,PW = __________.
```

This command makes the permanent file PREDICTEDRUN1 accessible as TAPE1, assuming that the correct password was specified after "PW = ". Similar commands will retrieve stored weather data.

In the simplest types of use, the user need not concern himself with these file issues: POEM automatically attaches the permanent file "WTHRSTATSNEW" if the weather simulator is turned off, and the file "PWSMOIST2" if the soil moisture submodel is turned off. POEM also creates (if plotting option is on) the SPRAYDATES(TAPE2) and RAINAMOUNTS(TAPE3) files required by DATAPLT to plot the pesticide levels generated by this run (on TAPE1). Thus, the user need not perform explicit ATTACH commands if he is using data just generated by the model.

Note--if POEM is to be run after other programs (or POEM) have been run in the same session, the user must first release the files POEM will try to attach: namely, type:

```
RETURN, TAPE4, TAPE9.
```

File Conventions in POEM Programs

POEM may read: TAPE4 - weather data (which it attaches as WTHRSTATSNEW)
TAPE9 - soil moisture data (which it attaches as PWSMOIST2)

POEM creates (depending on options selected)
TAPE1 - pesticide levels
TAPE2 - spraydates
TAPE3 - rainamounts
TAPE11 - isopod non-breeding populations
TAPE12 - isopod breeding populations
TAPE13 - collembolan populations
TAPE14 - earthworm populations
TAPE15 - spider populations

DATAPLT (stored on file ORCHARDCALPLOT6) uses:
TAPE2 - spraydates
TAPE3 - rainamounts
(TAPE1 - predicted pesticide levels, to be plotted as solid line - optional)
(TAPE4 - predicted levels, to be plotted as dashed line - optional)
(TAPE5 - measured pesticide levels, to be plotted as vertical bars - optional)

ORGPLOT uses:

TAPES11-15 as shown above.

Users wishing to run these programs at other sites should replace the CDC-specific PROGRAM statements, which also control file access, with appropriate file-handling statements. In particular, in FORTRAN77, the standard OPEN statements could instead be used.

Addendum to Users' Manual

Notice

Due to lack of funds and consequent lack of computer and manpower resources, some features and options of POEM are untested and/or undebugged. While the bulk of the code required to exercise all of the options described here is written, and all subroutines have run at various times as independent units, the linking of some routines has not been completed. Known problems are listed below:

(Option 2)	Weather simulation--not operable. Weather information must instead be provided in a file (TAPE4).
(Option 12)	Soil transportation model--not operable. Pesticide levels in soil cannot be broken down by depth.
(Option 9)	Soil moisture model--not operable. Soil moisture information must be provided in a file (TAPE9).